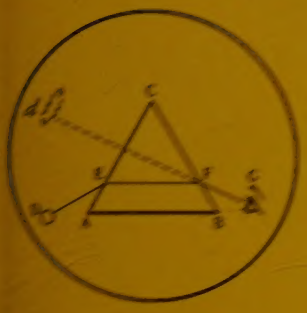

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DETERMINATION OF THE LIFETIME OF OPTICAL TRANSITIONS BY USING THE INTERFERENCE OF QUANTUM LEVELS

L. G. Zastavenko and O. A. Khrustalev (pp. 441-444)

Received 3 December 1960

A method is investigated for determining the lifetime of an excited state of an atom by observing the dependence of the resonance scattering of light in external fields on the strength of these fields.

Direct determination of the lifetime of an excited e is often difficult. In the present investigation, the ral width of levels is determined by measuring the nsity of the resonance scattering at a given angle as nction of the strength of the external fields applied e scattering medium. In essence, this method is d on the qualitative description of the phenomenon of ference in the case of partially overlapping of sub- ls given in ref. 1 (see also refs. 2 and 3). Section 1 isses the case in which the scattering atoms are in llel electric and magnetic fields; Section 2 describes nance scattering in the case when the levels of the ed state of the scatterer are split by the interaction een the electron shell and the nuclear spin in the ence of an external magnetic field.

1. Let us consider the resonance scattering of light oms in some excited intermediate state.* Let us

= present treatment is also applicable to other meth- of excitation of the atom (for instance, excitation by rons).

duce the following notations: τ is the lifetime of the ted atom, j is its (angular) momentum, m, the pro- on of this momentum on the z-axis, E_m, the energy e corresponding level, and A_m, the amplitude of the nance scattering which corresponds to this level. ssume that the intensity of radiation incident upon scatterer changes little in the energy range of in- st to us.

In the absence of external fields, all E_m are equal; amplitudes A_m are therefore additive, so that the rential cross section of the resonance scattering is n by the expression

$$W=\left|\sum_{m=-j}^{j} A_m\right|^2. \qquad (1)$$

Let us apply a strong* magnetic field to the scatter-

r our present purposes, we will call a field strong if splitting of levels with different m caused by the l considerably exceeds the natural width of the ex- d level, i.e.,

$$\tau|E_{m_1}-E_{m_2}|\gg\hbar, \qquad m_1\neq m_2. \qquad (2)$$

species. The level will split into 2j + 1 sublevels ted symmetrically relative to the m = 0 level. The ributions of the excited atomic states with different re additive without interference in this case, so that cross section for resonance scattering is

$$W=\sum_{m=-j}^{j}|A_m|^2. \qquad (3)$$

Next, we also apply an electric field to the scattering species in the direction of the z-axis. The electric field shifts the levels with the projections m and −m by equal amounts. It is therefore apparent that one can select the strength of the fields in such a manner that some of the levels with different m will coincide; i.e., $E_{m_1}=E_{m_2}$ for $m_1\neq m_2$. The contributions of these states to the resonance scattering will then interfere with each other, so that the cross section for scattering will be given by the formula

$$W=|A_{m_1}+A_{m_2}|^2-|A_{m_1}|^2-|A_{m_2}|^2+\sum_{m=-j}^{j}|A_m|^2. \qquad (4)$$

When one of the fields changes, the coincidence of the levels is destroyed. When this disruption reaches such a magnitude that condition (2) holds for all m_1 and m_2, the scattering cross section is again given by Eq. (3).

Thus, the dependence of resonance scattering on the magnetic field for a fixed electric field is given by a curve whose values are constant everywhere except in regions which correspond to a partial overlapping of levels with different m; in these regions the curve has narrow extrema (see ref. 3).*

*The intensity curve has a similar extremum at the zero values of the fields, when the application of the latter leads to a gradual splitting of initially coinciding levels. Equation (1) then becomes Eq. (3). Essentially, it is this phenomenon that is used in experiments with the so-called magnetic depolarization of the resonance scattering of light (see, for instance, ref. 4).

The shape of the curve in the vicinity of these extrema can be determined from the following simple considerations. Let us assume that there is an interference between two levels with the energies E_1 and E_2. The matrix element of resonance scattering in second order perturbation theory then has the form

$$A\left[1+i\frac{2\tau}{\hbar}(E-E_1)\right]^{-1}+B\left[1+i\frac{2\tau}{\hbar}(E-E_2)\right]^{-1}, \qquad (5)$$

where A and B are (generally speaking) certain complex numbers which depend on the nature of the levels, the state of polarization of the light, and the scattering angle.* The intensity of the scattered light is

*Because the splitting is small, the lifetimes of different sublevels can be considered identical.

$$\frac{W}{W_0}=1+\frac{2\,\mathrm{Re}\,(AB^*)-2\,\mathrm{Im}\,\dfrac{(AB^*)\,\tau(E_1-E_2)}{\hbar}}{W_0\left\{1+\left[\dfrac{\tau(E_1-E_2)}{\hbar}\right]^2\right\}},$$

where W_0 is the intensity of scattering far away from

the extremum. For certain angles and states of polarization of the incident and scattered light, the numbers A and B may have the same phase. Then the intensity in the vicinity of the extremum is*

*In the general case, when the phases of A and B are different, this expression gives the half-sum of the intensities at points which are symmetrically situated with respect to the extremum.

$$\frac{W}{W_0} = 1 + \frac{2|AB|}{W_0\left[1 + \frac{\tau^2 (E_1 - E_2)^2}{\hbar^2}\right]}, \qquad (6)$$

The width of the curve is determined entirely by the natural width of the line and the magnetic moment of the electric shell (g-factor). This results directly in the possibility of an experimental determination of the lifetime τ.

It is essential to note that the movement of atoms and the resulting Doppler shift do not affect the situation considered above. To observe this effect, it is therefore sufficient to have an electric field which shifts the levels of the excited atoms by an amount which is greater than the natural width of these levels, but not greater than their "Doppler" width. It should also be mentioned that for this effect to occur it is essential that no changes in orientation of the atomic momenta occur due to collisions (low pressure).

As a concrete example, let us assume that the ground state of the scattering atom has the momentum 0, and the excited state which is responsible for the resonance scattering, the momentum 1. Let $\mathbf{n}_0$ be the unit vector in the direction of the fields and $\mathbf{n}_1$ and $\mathbf{n}_2$ the unit vectors in the direction of the initial and final photons, respectively.

For a given strength of the electric field, one can choose the strength of the magnetic field $H = H_0$ in such a way that the levels with $m = 0$ and $m = -1$ (or $m = 1$) will coincide. An elementary calculation shows that for the scattering of unpolarized light, with $\mathbf{n}_0\mathbf{n}_1 = \mathbf{n}_0\mathbf{n}_2 = 1/\sqrt{2}$, $\mathbf{n}_1\mathbf{n}_2 = 0$, the dependence of the differential cross section on the value of H, with $H = H_0$, is

$$\frac{W}{W_0} = 1 + \frac{0.18}{1 + \frac{g^2\tau^2 (H - H_0)^2}{\hbar^2}}. \qquad (7)$$

2. In this section, we shall consider the splitting of the excited atomic level caused by the interaction of the electron shell with the nucleus (hyperfine structure), which has essentially the same effect as the electric field in Section 1.

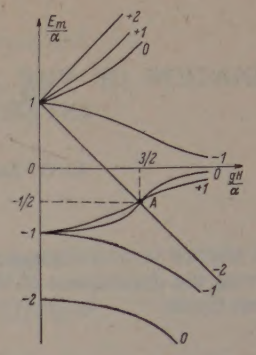
For an example, we shall consider an atom whose ground state has the orbital momentum $J = 0$. The orbital momentum of the excited state is $J = 1$, and the moment of the nucleus is also $I = 1$. The energy operator of the excited atomic state in the magnetic field is

$$a\mathbf{IJ} + g\mathbf{JH}. \qquad (8)$$

where α is the hyperfine structure constant and g is the gyromagnetic ratio of the electron shell (we disregard the interaction between the nucleus and the magnetic field).

The dependence of the eigenvalues of this operator on H is given schematically in the figure. The number near each curve indicates the projection of the momentum of the corresponding state on the field direction.

By way of orientation, we shall note that for $H \to 0$, the five upper levels merge into one with a total momentum of 2, and the three middle ones into one with a total momentum of 1; the lower one corresponds to the total momentum 0. For larger H, the three upper levels correspond to the projection 1 of the momentum of the electron shell, the three middle ones to the projection 0, and the three lower ones to the projection -1.



The levels with the projections -2, 0, 1 intersect at point A. Let the vectors $\mathbf{n}_i$ be connected by the relationships $\mathbf{n}_0\mathbf{n}_1 = \mathbf{n}_1\mathbf{n}_2 = \mathbf{n}_2\mathbf{n}_0 = 0$. As was shown in Section 1, point A corresponds to the extremum of the cross section of the resonance scattering for a given angle. However, in this case (in contrast to that of Section 1) the dependence of the matrix element (5) on the magnetic field is not confined to the denominator, because the numbers A and B themselves depend on the magnetic field. However, if $\alpha\tau \ll \hbar$ (i.e., if the natural width is much smaller than the hyperfine splitting), they change very little in the $\tau g\Delta H \sim \hbar$ region and the dependence of the intensity of resonance scattering in the vicinity of the extremum is therefore given by an expression similar to Eq. (6).*

*Our selection of directions corresponds to the real values of A and B.

Although three levels intersect in the point A, there will only be interference between the levels with the projections -2 and 0 (if only dipole transitions are considered).

The dependence of the cross section on H at $H = H_0$ has the form

$$\frac{W}{W_0} = 1 + \frac{a}{1 + \frac{\tau^2 g^2 (H - H_0)^2 \cdot 2.56}{\hbar^2}}.$$

For unpolarized light $a = 0.04$. If the incident and observed light are linearly polarized perpendicular to the field, then $a = 0.20$.

In conclusion, we express our gratitude to M. I. Podgoretskii on whose suggestion this work was undertaken.

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DETERMINATION OF THE MEAN TIME SPENT BY THE ATOMS, AND OF THE DIFFUSION COEFFICIENT IN THE PLASMA OF THE ARC DISCHARGE

B. M. Gol'dfarb and E. V. Il'ina (pp. 445-451)

Received 19 November 1960

High-speed motion pictures were taken of an arc discharge into which $NaNO_3$, $BaCO_3$, and Li_2CO_3 were introduced. Diffusion coefficients and the time spent by the Li, Na, and Ba atoms in the discharge were determined.

In order to understand the mechanism underlying ges in the atomic concentration of the substance analyzed, it is necessary to know the mean time by atoms in the plasma, or the diffusion coeffi-. A preliminary estimate of these quantities can tained by considering a simple model of the arc arge. We assume that:

1) the region in which the excitation of atoms and mission of light occur is a sphere of radius R;
2) the temperature within the sphere is constant rops sharply to the temperature of the surrounding um at r = R;
3) the concentration of atoms of the substance being zed is small compared to the total concentration of s in the discharge;
4) in the center of the sphere there is a source of bstance of a constant intensity α;
5) the radial electric field and the convection proc- do not affect the exit of the substance from the arge.

n order to determine the time dependence of the ntration of the substance in the discharge, one solve the diffusion equation

$$\frac{dN}{dt} = D\Delta N. \qquad (1)$$

N is the number of atoms and D is the diffusion icient of the atoms of the substance in question in which is a constant in our discharge model.

The diffusion coefficients of vapors of some metals been determined experimentally at temperatures of 2000°K (flame).[1-4] No measurements have been at higher temperatures.

Theoretical calculation of the diffusion coefficient h temperatures is very difficult, because under conditions, when repulsive forces are predominant, possible to describe interaction potentials and de- ine gas-kinetic diameters only for molecules and s with saturated electron shells.

The diffusion coefficient can be calculated approxi- ly according to Arnold's formula[5]

$$D = \frac{0.00837\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^{1/2} T^{3/2}}{(V_1^{1/3}+V_2^{1/3})^2 (T+C)}, \qquad (2)$$

M_1 and M_2 are the molecular weights of the undergoing diffusion, V_1 and V_2 are the molecular nes of the liquids at the boiling point (the values of re proportional to the gas-kinetic molecular diame- . T is the temperature (in °K), and C is the Suther- constant for the gas pair calculated according to the ula

$$C = \left(\frac{2\sqrt{V_1^{1/3}V_2^{1/3}}}{V_1^{1/3}+V_2^{1/3}}\right)\sqrt{C_1C_2}.$$

The values of C determined experimentally for Hg, Zn, and Cd[6,7] are 942, 1053, and 876°, respectively.

It can be concluded from comparison of the experimental and the theoretical data that Sutherland's temperature dependence formula

$$\frac{D}{D_0} = \left(\frac{C+T_0}{C+T}\right)\left(\frac{T}{T_0}\right)^{3/2}$$

is acceptable when the value of C/T amounts to a few tenths. According to this criterion, one can apply Sutherland's formula for the diffusion of metal atoms at temperatures of several thousand degrees.

The values of D in air at 5000°K and normal pressure are given for several metals in Table 1. For nitrogen and oxygen, the weighted mean values of the gas-kinetic diameters of the atoms and molecules of N and N_2, O and O_2 are taken. The degree of dissociation of these gases in the arc can be determined with fair accuracy[8] by calculating the equilibrium constant from the known heats of dissociation and the molecular dimensions. For N_2 and O_2 we obtain 42 and 97%, respectively.

Table 1

Metal	Li	Cu	Na	Zn	Hg	V	Tl	Sl	Sn	Pb	Cs	Ba
$V\left(\frac{cm^3}{gm\ mole}\right)$	2,52	2.52	3,14	2,73	2.67	3,18	3.27	3,18	3.47	3.64	4,22	4.52
$D\left(\frac{cm^2}{sec.}\right)$	42	24	23	22	21	20	19	17	16	15	14	12

It should be noted that since ionization and recombination occur very frequently in the arc (time for establishing of equilibrium is about 10^{-8} sec), each particle must be characterized by a diffusion coefficient which is a weighted mean value of the diffusion coefficients of the atom and the ion. Therefore, the calculations given above are valid if the gas-kinetic diameters of ion and atom are similar, or if the ionization coefficient is small.

The solution for an infinite medium with constant properties can serve as an approximate solution of Eq. (1) for the assumed model of the discharge.

$$N(r,\ t) = \frac{\alpha N_0}{4\pi Dr}\left[1-\Phi\left(\frac{r}{2\sqrt{Dt}}\right)\right]. \qquad (3)$$

The dependence of the number of atoms in the discharge on time is obtained by integrating expression (3) over the volume of the sphere

$$N_p = \int_v c(r,\ t)\,dv = N_1 - N_2, \qquad (4)$$

where

$$N_1 = N_\infty = \int_v \frac{\alpha}{4\pi D r}\, dv = \frac{\alpha R^2}{2D} \qquad (5)$$

gives the number of atoms in the discharge for $t \to \infty$ and

$$N_2 = \frac{\alpha}{D}\left\{\frac{\Phi\left(\frac{R}{2\sqrt{Dt}}\right)}{2}[R^2 - 2Dt] + \frac{R2\sqrt{Dt}}{2\sqrt{\pi}}\, e^{-\frac{R^2}{4Dt}}\right\}. \qquad (6)$$

The function $N_p(t)$ for D = 20 cm²/sec is depicted in Fig. 1. The time required for the concentration of atoms in the discharge to reach half of the limiting value N_∞ is 0.003 sec. Formula (5) gives the connection between the rate of evaporation of the sample, the conditions of the discharge (its temperature, which governs the coefficient of diffusion), the dimensions of the cloud, and the number of atoms in the discharge.

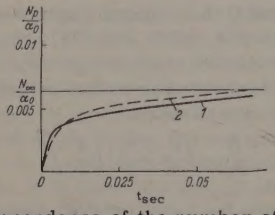

Fig. 1. Dependence of the number of atoms in the discharge on time, for an unlimited sample. Curve 1—calculated according to Eq. (4); curve 2—according to Eq. (7).

A similar, but simpler, $N_d(t)$ function can be obtained on the assumption that the number of atoms leaving the discharge during the time dt is proportional to the number of atoms present in the discharge at a given moment:

$$dN_1 = \beta N(t)\, dt,$$

where "the exit coefficient" β is a quantity which is reciprocal to the mean time τ_1 spent by the atoms in the discharge: $\beta = (\ln 2)/\tau_1$. For a constant rate of evaporation, the number of atoms entering the discharge in the time dt is $dN_B = \alpha N_0 dt$, where αN_0 is the rate of evaporation.

The change of the number of atoms in the discharge

$$dN_d = dN_B - dN_1 = \alpha N_0 dt - \beta N(t)\, dt.$$

From this we obtain

$$N_d(t) = \frac{\alpha N_0}{\beta}(1 - e^{-\beta t}). \qquad (7)$$

The condition that N_∞ in (5) must equal N_∞ in (7) gives us

$$\beta = \frac{2D}{R^2}, \quad \tau_1 = \frac{R^2}{2.9D}. \qquad (8)$$

An estimation of the diffusion rate shows that high-speed motion picture photography can be used for the experimental study of this process.

1. Motion pictures of the arc discharge were taken with an SKS-1 motion picture camera at a rate of 500 to 3000 frames/sec.

A 5 amp dc arc with carbon electrodes was used; the electrode gap was 8 mm. The arc was triggered with the high-voltage circuit of a PS-39 source. The substances under investigation—$NaNO_3$, $BaCO_3$, and Li_2CO_3*—wer

*The substances were chosen with a possibly large di ference with respect to diffusion coefficient and with lines that are conveniently separated by means of inte ference light filters.

introduced into discharge on the point of a quartz nee in the form of a granule with a diameter of 0.1 and 0. mm.

The needle was placed in the middle of the gap be the arc was started, or was fastened to the shaft of a Warren SD-60 motor. In the latter case, the point of needle swept through the discharge at a velocity of 60 cm/sec. The exposure was synchronized with the pas sage of the needle through the discharge by means of moving contact situated on the shaft of the same moto The camera was started and the exposure time con- trolled by means of a relay operated by the same mov contacts. A diagram of the arrangement is shown in Fig. 2.

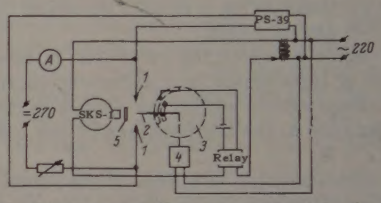

Fig. 2. Diagram of the arrangement. 1—arc electrodes; 2—quartz needle; 3—contact arrangement; 4—Warren motor, 5—interference filter.

In order to separate the region in which the adde substance emitted light from the general background the arc, the exposures were made through interferen filters. The transmission maxima of the filters were selected in the vicinity of the lines Na 5890 A, Li 610 A, and Ba 6142 A; the half-widths of the transmissio maxima were 80 to 120 A.

The pictures were made with 16 mm Panchrom motion picture film. The objective lens of the movie camera could be extended toward the object by means an extension tube, which made it possible to obtain th arc pictures at 1/3 natural size.

2. Figure 3 shows one of the frames of the arc p tures made at 500 frames/sec without a filter and wi out introducing any material on the needle.

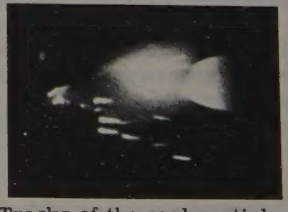

Fig. 3. Tracks of the coal particles in the arch category.

The velocity of the convection currents can be d termined from the camera speed and the length of th tracks of the carbon particles flying out of the anode An average value, determined from several similar tures, is 70 cm/sec. A comparison with the diffusio data given below shows that convection is not a facto determining the time spent by the atoms in the disch

he evaporation of an 0.1-0.3 mm granule from the t of a stationary needle begins 0.005 to 0.01 sec after starting of the arc and lasts for 0.1 to 0.2 sec. The ease in the intensity of emission is determined not he substance leaving the discharge, but by the evap- ion of the material.

In order to limit the evaporation time, measurements e made with a moving needle.

Figures 4 to 6 show a series of frames of the films hich the evaporation from a moving needle was photo- hed. The inspection of 25 similar films gives the owing picture of the process:

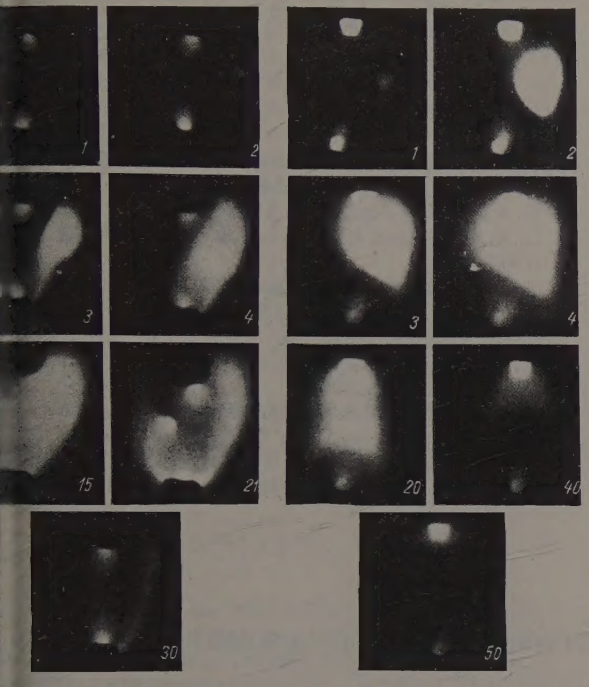

Fig. 4 Fig. 5

Fig. 4. Change of the appearance of the luminous region with evaporation from a moving needle. Na (1000 frames/sec).
Fig. 5. Same as Fig. 4, Li (3000 frames/sec).

(a) The evaporation of the substance begins several sandths of a second after the end of the needle hes the discharge region (more precisely, the re- where the luminescence of the vapors of the sub- ce introduced is going to take place).

(b) The luminous region appearing around the grain aterial spreads faster in the direction of the cathode.

(c) By the time the luminescence fills the whole gap, end of the needle has left the discharge, and the dissi- on of the cloud has begun.

(d) The substance lasts longer in the region close to cathode; this region remains luminescent for about sec after the dissipation of the main part of the cloud.

(e) During the dissipation of the cloud, the most in- e luminescence (and, possibly, the greatest concen- ion of neutral atoms) is observed not on the axis, but ne peripheral parts of the discharge.

(f) The evaporation of the substance often occurs in or three stages. Between the moments of maximum ssion there is a complete or partial departure of the stance from the discharge region.

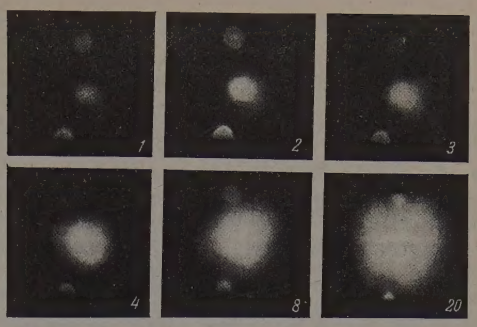

Fig. 6. Same as Fig. 4, Ba (3000 frames/sec).

The irregularity of the evaporation process, the nonuniformity of the discharge plasma with respect to evaporation conditions, the variation of thickness of the emitting layer of the substance, and a number of other causes permit only a very rough determination of the features of the diffusion process.

Figure 7 shows typical curves of the change of optical density from frame to frame. Measurements were made with a narrow photometer diaphragm which isolated the region of maximum density (photometry with a diaphragm which covers the whole discharge region gave similar results). Approximating the descending branches of the curves by an exponential function $\exp(-0.7t/\tau_1)$ made it possible to determine the mean time τ_1 the atoms stayed in the discharge.

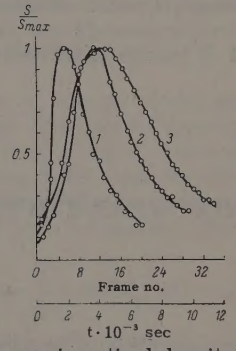

Fig. 7. Change in optical density of the discharge image (3000 frames/sec). Curve 1—Li; curve 2—Na; curve 3—Ba.

Table 2 gives the average of 3 to 5 τ_1 values for each element along with the extreme values. The values of the diffusion coefficient (D_1) calculated according to formula (8) are also given (R is assumed to be 4 mm).

Table 2

Metal	τ_1 (sec)	D_2 (cm²/sec)	D_1 (cm²/sec)
Li	0,002 (0,0014—0,0027)	28	40
Na	0,003 (0,0022—0,0039)	19	21
Ba	0,005 (0,0037—0,0060)	11	13

4. Another method of determining D is based on measuring the velocity of the edge of the luminous cloud, or of a surface of a given intensity of luminescence. Figure 8 depicts changes in density along the diameter of the image of the luminous region from several consecutive frames. The shape of the curves and the relative distances between the curves corresponding to con-

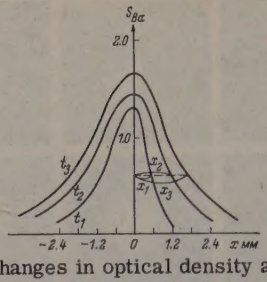

Fig. 8. Changes in optical density along the diameter of the image of the luminous region, Ba. $t_1 = 0$, $t_2 = 0.002$ sec, $t_3 = 0.004$ sec.

secutive instants in time confirm the diffusion nature of the process.

The diffusion coefficient can be determined approximately according to the formula

$$x_{n+1}^2 - x_n^2 = 2D(t_{n+1} - t_n),$$

where x_n and x_{n+1} are the abscissas of the curves which correspond to the times t_n and t_{n+1} for equal optical density. The results of the determination made by this method are given in Table 2 (D_2).

When the inaccuracy of the theoretical determination and the possible systematic experimental errors are taken into consideration, the agreement between the theoretical and experimental values of D should be considered as satisfactory.

In a recently published work,[9] similar values of diffusion coefficient were obtained (if one disregards Li, for which a value of D was found that does not fit the functional dependence on atomic weight which was obey by the other elements); however, this agreement is the result of mutual cancelling of the differences in the va of τ_1 and the values of the numerical coefficient in the formula connecting D and τ_1. It seems that the determination of D is less reliable by means of τ_1 than by the velocity of displacement of the edge of the luminou region, in which case the results do not depend on an i defined "discharge radius," or on the choice of the m for calculating the diffusion rate (connection between and τ_1). In order to increase the accuracy of the meas urement of D by the latter method, it is necessary to use a speed of the order of 20,000 frames/sec and to u a more uniform and extended light source.

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NONADIABATIC TRANSITIONS NEAR THE TURNING POINT IN ATOMIC COLLISIONS

E. E. Nikitin (pp. 452-456)

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The probability of nonadiabatic transitions near the turning point was calculated for a two-atom system by the theory of nonstationary perturbations assuming wide and narrow splitting of terms, respectively.

The probability of a number of intramolecular and intermolecular nonadiabatic processes is usually calculated by the Landau-Zener[1] formula. In its derivation, either the quasi-classical wave functions of the nuclei[2] or the theory of nonstationary perturbations[3] is used, it being assumed that the point of quasi intersection of terms is far from the turning point of the relative motion of the nuclei. This limits the useful range of the formula for describing charge exchanges, nonradiative transitions, and other nonadiabatic processes near the threshold. The probability of a nonadiabatic transition near the turning point can be calculated using Airy functions as nuclear wave functions (see ref. 1, p. 360). It is not difficult to show (see below) that the condition of applicability of first order perturbation theory frequently appears to be violated, so that it is even necessary to take account of the difference in the terms in the zeroth approximation.

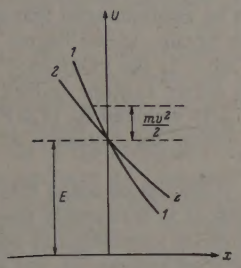
In the present paper the probability for a nonadiabatic transition near the turning point is calculated for a two atom system by the theory of nonstationary perturbati for the cases of wide and narrow splitting of terms.

At small splitting, the perturbation causing this splitting need not be taken into account in the zeroth ap proximation. Then, in the first approximation of the th ory of perturbations, the nonstationary problem can be solved by considering the motion of the nuclei classica To make this possible, it is first of all necessary that near the turning point the difference between the effec forces acting on the nuclei in the two electron states b small compared to the forces themselves, i.e., $\Delta F = |F_1 - F_2| \ll F_1, F_2$.

The inequality $\Delta F/F \ll 1$ is analogous to the con tion of the proximity of states when the quasi-classica matrix element between these states reduces to the Fourier component.[1] Such a case is shown in the figur The motion of the nuclei near the turning point is de- fined by the classical trajectory

$$x=\frac{F}{2m}t^2-\frac{mv^2}{2F}, \qquad (1)$$

e m is the effective mass of the nuclei, x is the nce measured from the point of intersection, v is elocity at that point, and the time t = 0 corresponds e turning point. Force F is some average value be- n F_1 and F_2. Now it should be noted that the exact ability of transition, calculated without introducing oximate classical motion of the nuclei, must be a netrical function of F_1 and F_2. This means that the itude of F, on which, through Eq. (1), the approxi- probability of the transition will depend, must also symmetrical function of F_1 and F_2. Then, it is ible to approximate $F \simeq \frac{1}{2}(F_1+F_2) \simeq (F_1F_2)^{1/2}$ to n an accuracy of terms of the order of $(\Delta F)^2/F$. The nce of the correction term which is linear in ΔF ap- s to be important, and considerably increases the racy of the calculations.



The probability of the transition in the first approxi- on is

$$P_{12}=\frac{1}{\hbar^2}\left|\int\limits_{-\infty}^{\infty} a\exp\left[\frac{i}{\hbar}\int^{t}(U_1-U_2)\,dt\right]dt\right|^2, \qquad (2)$$

e U_1 and U_2 are the intersecting terms. Assuming $U_1 - U_2 = \Delta Fx$ and that the matrix element a of the iabatic interaction is weakly dependent on t, the ral (2) can be expressed by the Airy function. It is fficult to show that P_{12} coincides with the results exact quantum-mechanical calculation[1] when $\ll 1$. Omitting the computation and introducing the mensional parameters $\varepsilon = mv^2\Delta F/4aF$ and $b = a\sqrt{am/\Delta FF}$, we obtain

$$P_{12}=\pi b^{4/3}\Phi^2(-\varepsilon b^{2/3}). \qquad (3)$$

extremely large negative and positive values of the endent variable of the Airy function, this expres- gives us

$$P_{12}=\begin{cases}\dfrac{\pi}{2}\dfrac{b}{\sqrt{\varepsilon}}=\dfrac{4\pi a^2}{\hbar v\Delta F}, & \varepsilon b^{2/3}\gg 1\\ \dfrac{\pi}{4}\dfrac{b}{\sqrt{|\varepsilon|}}\exp\left[-\dfrac{4}{3}b|\varepsilon|^{3/2}\right], & \varepsilon b^{2/3}\ll -1,\end{cases} \qquad (4)$$

The rapidly oscillating probability was averaged the small energy interval in the first of these equa- . The opposite condition $|\varepsilon b^{2/3}| \ll 1$ corresponds to ase in which the turning point and the intersection approach each other. Then $\Phi^2(-\varepsilon b^{2/3}) \sim 1$, and the ability of the transition appears to be of the order $b^{4/3}$. To find the region of inapplicability of the first oximation, we evaluate the parameter b from the r side, approximating the potential of interaction by xponential function with a radius of action equal to F is then approximately equal to $\mathcal{E}\alpha$, where $\mathcal{E}$ is otential energy at the point of intersection, so that the following inequality is obtained for b

$$b=\frac{4a^{3/2}\sqrt{m}}{\hbar F}\sqrt{\frac{F}{\Delta F}}>\frac{(2a)^{3/2}}{\mathcal{E}}\sqrt{\frac{2m}{\hbar^2a^2}}. \qquad (5)$$

On the other hand, α can be evaluated on the basis of Morse's potential for stable states of diatomic molecules. This evaluation gives $\sqrt{2m/\hbar^2a^2} \simeq N/\sqrt{D}$, where D is the dissociation energy and N is the vibrational quantum number, so that we finally obtain $b > N(2a)^{3/2}/\mathcal{E}\sqrt{D}$. It should be noted that if one or both of the potential curves represent long range forces (collision of ions, resonance interaction of normal and excited atoms, etc.), this inequality increases. For a numerical evaluation of b, the energies $\mathcal{E}$ and D can be taken to be of the order of a few electron volts, and $N \sim 10^2$. When terms of the same symmetry interact (typical case of charge exchange), the term splitting energy a can be as high as 1 ev.[4] Large values of 2a are also to be expected in predissociation as a result of the convergence of terms of the same symmetry. Although these cases are infrequent, some have been detected.[5] It is not difficult to see that, under these conditions, b can be of the order of 10, which makes the first approximation leading to (3) inapplicable.

To determine the probability of the transition at large values of b (wide splitting), it is necessary in the zeroth approximation to start with correct adiabatic functions ψ_1, which are found when splitting is taken into account. These functions are expressed as linear combinations of unperturbed functions φ_i

$$\left.\begin{aligned}\psi_1&=[\varphi_1\cos\chi+\varphi_2\sin\chi]\exp\left(-\frac{i}{\hbar}\int E_1dt\right),\\ \psi_2&=[-\varphi_1\sin\chi+\varphi_2\cos\chi]\exp\left(-\frac{i}{\hbar}\int E_2dt\right),\quad \chi=\frac{1}{2}\operatorname{arctg}\frac{2}{y},\end{aligned}\right\} \qquad (6)$$

where $y = \Delta Fx/a$, E_1 and E_2 are the terms when splitting is considered. The nonadiabatic function Ψ is sought in the form of $C_1(t)\psi_1 + C_2(t)\psi_2$. The solution from the first approximation of the corresponding system of equations for the coefficients $C_i(t)$ with initial conditions $C_1(-\infty) = 1$ and $C_2(-\infty) = 0$ has the form

$$C_2(\infty)=\int\limits_{-\infty}^{\infty}\dot{\chi}\exp\left[\frac{i}{\hbar}\int^{t}(E_1-E_2)\,dt\right]dt. \qquad (7)$$

Substituting $E_1 - E_2 = \sqrt{4a^2+(\Delta Fx)^2}$ into Eq. (7) and changing the variable of integration, we obtain

$$C_2(\infty)=\int\limits_{-\infty}^{\infty}\frac{\xi}{1+(\xi^2-\varepsilon)^2}\exp\left(ib\int\limits_0^{\xi}\sqrt{1+(z^2-\varepsilon)^2}\,dz\right)d\xi. \qquad (8)$$

For an approximate calculation of integral (8), it is possible to use the Landau method.[1] The path of integration of (8) is shifted into the upper half-plane of the complex variable ξ to the nearest singularity of the integrand ξ_0. In our case, there are four points of this kind; they are located symmetrically with respect to the real and imaginary axes and correspond to the branch points of the exponential function. In this way, we obtain

$$P_{12}\sim\exp\left[2\operatorname{Re}\left(ib\int\limits_0^{\xi_0}\sqrt{1+(z^2-\varepsilon)^2}\,dz\right)\right]. \qquad (9)$$

The factor preceding the exponential term, which depends weakly on ε, can be determined approximately for individual values of ε. Integral (9) can be expressed by total elliptical integrals of a complex modulus, which permits accurate calculation of its value. But of greater

interest are its approximate expressions in various regions of ε.

At large ε values, $\arg\sqrt{i+\varepsilon}$ appears to be the small parameter of the expansion of the integral so that, after appropriate calculations, we obtain

$$P_{12}\sim\exp\left[-\frac{\pi}{4}\frac{b}{\sqrt{\varepsilon}}\left(1+\frac{0.031}{\varepsilon^2}-\frac{0.0002}{\varepsilon^4}+\ldots\right)\right]. \quad (10)$$

The series in parentheses converges very rapidly and can be used for evaluation even at $\varepsilon < 1$. The factor preceding the exponential term in (10), for $\varepsilon \gg 1$, is obtained by comparing this expression with the Landau-Zener formula, and is equal to 2.

In the region $|\varepsilon| \ll 1$ the series can be expanded in $(\pi/4) - \arg\sqrt{i+\varepsilon}$, which gives

$$P_{12}\sim\exp\left[-\frac{\pi}{4}b\,(1.57-1.11\varepsilon+\ldots)\right]. \quad (11)$$

Finally, for $\varepsilon \ll -1$, we obtain

$$P_{12}\sim\exp\left[-\frac{4}{3}b\,|\varepsilon|^{3/2}+\ldots\right]. \quad (12)$$

In the last case, the angle $\varphi = (\pi/2) - \arg\sqrt{i+\varepsilon}$ appears to be the small parameter of the expansion, and when $\varphi \to 0$, integral (9) is not an analytical function of φ. The corrections, which are related to nonanalytic terms in (12), can be calculated by the following method: It is physically clear that for large negative values of ε, when a nonadiabatic transition takes place by tunneling below the point of quasi intersection, both of the initial zero approximations used above must lead to the same result in the first approximation. Then, the comparison of (12) and (4) shows that the factor preceding the exponential term in (12) is approximately equal to $(\pi/4)/(b/\sqrt{|\varepsilon|})$.

The expansions (10)-(12) permit the determination of the dependence of the transition probability on the energy near the threshold. The corrections for the Landau-Zener formula, which take account of the first term of the expansion in (10), become appreciable at $\varepsilon \sim 1/2$. This corresponds to relative energies of the order of $aF/\Delta F$ at the quasi-intersection point. Since the splitting 2a can be significant and $F/\Delta F$ appears to be the large parameter, the threshold region can be fairly wide and accessible to experimental detection. As $F/\Delta F$ decreases, the derived expressions become less accurate. But, since the threshold region narrows, the probability in the whole interval of energies can still be determined with greater accuracy by the Landau-Zener formula.

During kinetic collisions of the gas, the nonadiabatic transition near the point of intersection at small splittings ($b \ll 1$) appears to be significant when $\mathcal{E} \gg kT$, and when $\varepsilon b^{2/3} \leq 1$ in an interval of energies of the order of kT near the threshold. An evaluation similar to the one given above shows that this occurs at

$$\left(\frac{\Delta F}{F}N\right)^{2/3}\frac{kT}{\mathcal{E}^{2/3}D^{1/3}} \lesssim 1.$$

When $\Delta F/F \sim 1/5$ and $N \sim 10^2$, for instance, the reduc condition can be written in the form $kT/\mathcal{E} < 1/10$.

For wide splittings ($b \gg 1$), the transition near th turning point is important when the dependence of P_{12} the energy at $\varepsilon \ll 1$ is weaker than the variation of th Boltzman factor (when $\varepsilon\beta \ll mv^2/2kT$). This inequali is satisfied for $a \gg (\Delta F/F)kT$.

In expressions (2) and (7), the dependence of the w functions φ on time was not taken into account. This d pendence is determined by the parametric dependence the wave functions on the coordinates of the nuclei. Mordvinov and Firsov[6] showed that, for nonadiabatic transitions far from the turning point, the calculation such a dependence increases the square of the matrix element of perturbation by $\sim\hbar^2v^2(\varphi_1\partial\varphi_2/\partial x)^2$. Since $(\varphi_1\partial\varphi_2/\partial x)^2 \approx \alpha^2$, it is not difficult to show that the correction $\hbar^2v^2\alpha^2$ to a^2 is very small and the ratio $\hbar^2\alpha^2v^2/a^2 \approx Dmv^2/N^2a^2$ is much smaller than unity for wide interval of energies $mv^2/2$ near the threshold. However, it should be remembered that since the nonadiabatic transition occurs in the region defined by the condition $(\Delta F/\hbar)\int x dt \sim 1$, the relation $\hbar^2v^2\alpha^2 \ll a^2$ mu be satisfied in this entire region. In this case, the con dition $\hbar^2v^2\alpha^2/a^2 \ll 1$ is reduced to $(F/\Delta FN)^{2/3}$. $D^{4/3}\mathcal{E}^{2/3}/a^2N^2 \ll 1$, which, for example, at $\Delta F/F \sim 1/10$ gives $D^2/a^2 \ll 10^3$.

In conclusion, it should be noted that in investigat molecular collisions, it is frequently possible, in the zeroth approximation, to adiabatically separate not on the motions of electrons and nuclei, but also the vibra tional motion of the nuclei from the relative motion of molecules. The expressions obtained also retain their meaning in this case. However, the functions φ_1 and will refer to the vibrational states of the colliding mo cules. Since the adiabatic separation of various nuclei motions is derived with a lower accuracy than the sep tion of the motions of electrons and nuclei, it can be e pected that relatively wide splittings should occur mo frequently in molecular collisions than in atomic colli sions.

I wish to express my gratitude to N. D. Sokolov f discussions on this work.

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IE ELECTRONIC SPECTRA OF SIMPLE BENZENE DERIVATIVES AS A FUNCTION OF pH
II. The Absorption Spectra of Nitrobenzene and Nitrophenol

L. V. Smirnov and A. I. Suprunenko (pp. 457-464)

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The absorption spectra of solutions of nitro derivatives of benzene and of the nitrophenol isomers were investigated as a function of pH and solvent polarity. The absorption bands in the ultraviolet region of the foregoing compounds, and of some others similar to them, have been tabulated and identified.

RODUCTION

In a preceding paper[1] it was shown that the elec- c absorption spectra of undissociated hydroxyben- s exhibit in the region $\lambda > 200$ mμ only two bands, ted by us by B and C, which because of their posi- relative intensities, and behavior in various sol- s can be considered as the analogues of the benzene) and C(^1L_b) bands. A third band, denoted D, ap- s in the spectra of the bivalent o- and p-hydroxy- enes. It does not have an analogue in the benzene trum and is assigned to the n—π transition in ortho- paraquinoid structures. In the region $\lambda < 200$ mμ, extending down to the Rydberg frequencies, only one appears in the spectra of benzene derivatives. This (A) is the analogue of the benzene ^1B_b band.[2,3] The spectra of undissociated molecules of phenol dihydroxybenzene isomers can be considered as al of the mono- and disubstituted benzene deriva- s in which the substituent groups exert the type I nting effect. Examples of benzene derivatives where substituent groups exert the type II orienting effect examined below; these are mononitrobenzene (MNB), a-dinitrobenzene (m-DNB), and symm.-trinitroben- (s-TNB). The nitro-group because of its type II ori- g effect is a case of particular interest, as theoreti- alculations[4] show that the presence of a nitro group s to substantial changes in the energy level scheme e unsubstituted molecule. It is known experimentally a weak band appears on the long-wavelength side in spectra of nitro derivatives of benzene. The band has assigned to the nitro group in early investigations.[5] spectra of disubstituted benzenes, where the substitu- are groups having opposing orienting effects (type I II), have their own peculiarities, of which the most acteristic is the difference in the number of bands he spectra of the para-isomers on the one hand and spectra of the ortho- and meta-isomers on the other. examine below the spectra of the isomeric nitrophe- s as an example of this case.

A survey of the literature dealing with the spectra enzene derivatives shows that most of the investiga- s, however divergent in their aims (effect of position, ber and nature of the substituents,[6-14] solvent ef- ,[15-19] steric effects,[2,20-22] formation of complexes aromatic hydrocarbons,[23-26] dimerization,[27] dichro- of bands[28]), were based on a direct or indirect as- ption of a genetic relationship between the bands of zene and those of the benzene derivatives. There is, ever, no general agreement concerning the assign- t of the bands. There is not even agreement con- ing the number of bands in certain cases. There also o widely accepted designation of bands, as theoretical results necessary for the classification of electronic transitions in the spectra of benzene derivatives are available in only a few cases.

The designation A, B, C, D of bands beginning on the short wavelength side, used in the present paper, has been used previously by other authors[2] and by us in a preceding paper.[1] The various designations of bands in the spectra of benzene derivatives used over the last 20 years are summarized in Table 1.

Table 1

Compound	Bands				Literature
	178–180 mμ	185–205 mμ	230–270 mμ		
Benzene	—	*K*	*B*		[29]
	β	*P*	■		[30]
	—	Primary	Secondary		[6]
	^1B_b	^1L_a	^1L_b		[31]
	E_1	E_2	*B*		[32]
	A	*B*	*C*		[1]
	178–210 mμ	206–270 mμ	220–400 mμ	265–800 mμ	
Benzene derivative	—	*K*	*B*	*R*	[29]
	—	2	1	Vorbande	[5]
	A	*B*	*C*	*D*	[1, 2]
	—	Second primary	First primary	Secondary	[6]
	4	3	2	1	[27]
	—	3	2	1	[13]

EXPERIMENTAL PART

All spectra were measured using an SF-4 spectrophotometer. In order not to miss any possible band in the region $\lambda > 200$ mμ, the concentration of the solutions was varied from 5×10^{-5} to 2.4 M and the cell thickness from 10 to 2×10^{-4} cm. The solvents were water, aqueous solutions of NaOH and HCl, ethyl alcohol, and n-hexane. The latter was purified by passing through an Al_2O_3 column and checked spectroscopically for the absence of benzene. All the compounds were purified by distillation or recrystallization. The hexane solutions of the nitrobenzenes were passed through an Al_2O_3 column in order to remove any complexes between the nitrobenzenes and possible aromatic impurities and then checked spectroscopically for the absence of naphthalene and other polyacenes. The compounds synthesized by us were compared with samples obtained from other research institutes. The pH measurements were performed using an LP-57 potentiometer.

DISCUSSION OF RESULTS

Nitrobenzene. Figures 1-4 show the spectra of MNB, m-DNB, and s-TNB. The spectra of all three compounds

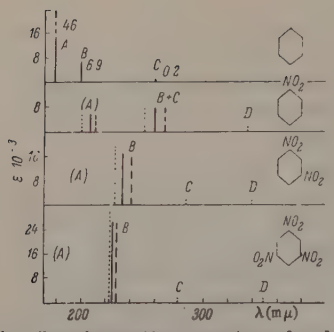

Fig. 1. The absorption spectra of solutions of benzene and nitrobenzenes in n-hexane (dotted line), ethyl alcohol (full line), and water (broken line).

in the range $\lambda > 200$ mμ exhibit an intense band which is "red-shifted" (shifted to longer wavelengths in going from a nonpolar to polar solvent) as indicated by the results presented in Table 2 and Figs. 2-4. The regular hypsochromic shift (Fig. 1) and additive increase in the intensity of the given band with increase in the number of nitro groups (in the ratio 1:2:3) does not leave any doubt that this band is of the same type in all three compounds. This band is designated the B-band.

It had been suggested earlier[6] that the foregoing band was the shifted B-band of benzene. However, some authors,[8] after correctly assigning it to the B-band in the MNB spectrum, assigned it to the A-band in the m-DNB spectrum assuming that there was an inflection in the latter spectrum in the region of 250 mμ. This inflection is indeed observed but in the spectrum of the benzene-s-TNB complex.[23] Since our hexane solutions of the nitrobenzenes were passed through an Al_2O_3 column, we did not observe any inflections in the 250 mμ region.

All three spectra exhibit in the long wavelength region $\lambda \approx 330$-360 mμ a weak ($\varepsilon_m \approx 150$-180(band designated D. This band does not have an analogue in the benzene spectrum. Because of this band's small intensity, position, and "blue" shift in going from hexane to a polar solvent, it must be assigned to the n—π transition. The breadth of the band and the proximity of the intense B-band preclude any reliable measurements of the shift of this band in various solvents. However, in the case of m-DNB, the band is best resolved in hexane solution ($\lambda \approx 340$ mμ), i.e., in the case where the intense

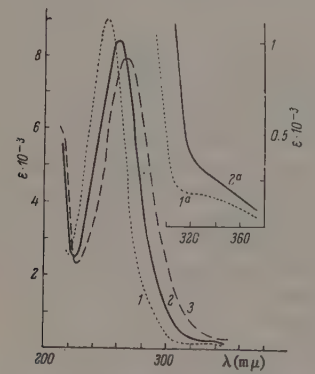

Fig. 2. The absorption spectra of solutions of mononitrobenzene (MNB) in n-hexane (curves 1, 1a), ethyl alcohol (curves 2, 2a), and water (curve 3).

Table 2

Compound	Solvent					
	MNB		m-DNB		s-TNB	
	λ_m (mμ)	$\varepsilon_m \times 10^{-3}$	λ_m (mμ)	$\varepsilon_m \times 10^{-3}$	λ_m (mμ)	$\varepsilon_m \times 10^{-3}$
Hexane	252	9	228	19.4	224	30.5
Ethyl alcohol	260	8.3	234	17.6	226	26.6
Water	268	8.1	242	16	230	26.8

B-band is shifted most towards shorter wavelengths. Hence the D-band either shifts in a direction opposite that of the "red-shifted" B-band or remains generally unaffected. The latter face as well as the position and low intensity of the D-band support its assignment to a n—π transition (according to ref. 6 this band occurs at 305 mμ in an aqueous solution of m-DNB, i.e., is "blue shifted").

In the region 270-300 mμ in the spectra of nitrobenzenes, between the B- and D-bands there occurs another band (inflection) designated C. This band, observed earlier,[5] is well-defined in the m-DNB spectrum (Fig. 3), broader in the case of s-TNB (Fig. 4), and is absent from the MNB spectrum (Fig. 2). The position of the C band is similar in the spectra of m-DNB and s-TNB. Hence it can be assumed that in the case of MNB the C band lies in the region 280-300 mμ and because of its low intensity is completely overlapped by the intense B-band (a point made previously in ref. 5).

Of particular interest is the presence of vibrational structure ($\nu = 1320 \pm 80$ cm^{-1}) in this band. This vibrational structure has no relation to the vibrational structure of the benzene C-band (Fig. 3, curves 3 and 3a). The position of the vibrational maxima were similar to those of the $P(^1L_a)$-band of naphthalene. In order to make sure that the observed phenomenon was real, we attempted (apart from purification by recrystallization

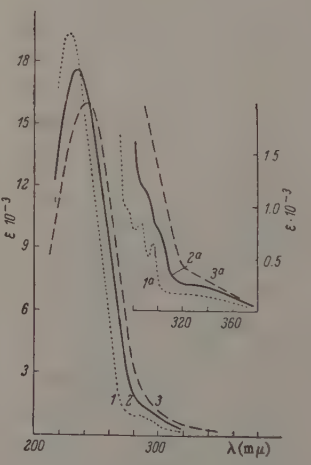

Fig. 3

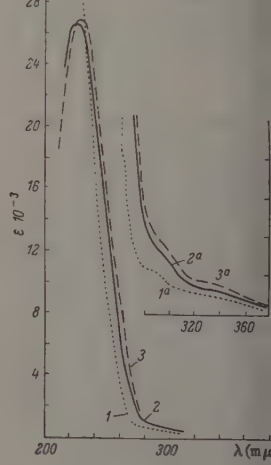

Fig. 4

Fig. 3. The absorption spectra of solutions of m-dinitrobenzene (m-DNB) in n-hexane (curves 1, 1a), ethyl alcohol (curves 2, 2a), and water (curves 3, 3a).

Fig. 4. The absorption spectra of solutions of symm.-trinitrobenzene (s-TNB) in n-hexane (curves 1, 1a), ethyl alcohol (curves 2, 2a), and water (curves 3, 3a).

chromatographic separation on an Al_2O_3 column) the limation of various samples of m-DNB (obtained from erent sources) at temperatures from 20 to 50°C. No iation was observed in the positions and intensities of vibrational components of the C-bands of the sub- ates and the remainders. Hence this vibrational struc- e must be assigned to the valence vibration of the -o group. The recently published[33] results on the man spectra of m-DNB support the foregoing conten- n.

The same three bands are observed in the spectra of ortho- and para-dinitrobenzenes as in the spectrum of DNB.[5] In the case of the B-band, λ_m-ortho < λ_m-meta < -para. Comparison of the spectra of analogous isomers itrobenzene and undissociated hydroxybenzenes show t the nitro group causes a larger bathochromic shift he bands than the hydroxy group and sharply increases intensity (ε_m) of the B-band relative to the C-band. he mono, 1,3- and 1,3,5-substituted benzenes, the in- sities of the B-bands are in the ratios 1:1:0.5 in the ctra of the hydroxybenzenes and 1:2:3 in the spectra he nitrobenzenes.

Nitrophenol. For the spectra of phenol derivatives taining substituents exerting a type II orienting ef- t, there is no agreement in the literature concerning number of bands and the interpretation of their be- ior (e.g., spectra of nitrophenol isomers[5,6,14]). In ne investigations weak bands were obviously missed g., in ref. 6—the 260 mμ region of the para-nitrophenyl on spectrum and the 290 mμ region of the m-DNB ctrum). From Figs. 5, 6, and 7 it is seen that all the ds in the spectra of the nitrophenol isomers experi- e a "red" shift in going from nonpolar to polar sol- ts. Isobestic points were obtained from the absorp- curves at various pH values. These points indicate existence of two (and only two) forms—dissociated undissociated molecules. The bands assigned by our thod are given in Table 3.

Table 3

Solvent	Band A		B		C		D	
	λ(mμ)	ε	λ(mμ)	ε	λ(mμ)	ε	λ(mμ)	ε
n-Hexane	—	—	(226)	(3000)	270	7300	346	3750
Water (pH=3)	(209)	(14800)	(226)	(3000)	278	6400	351	3000
0.02N aq. NaOH	228	14600	(250)	(4000)	282	4100	416	4500
n-Hexane	—	—	228	11300	266	7250	326	2780
Water (pH=3)	208	(1300)	228	9900	274	7700	330	2560
0.5N aq. NaOH	226	19200	252	14500	292	6000	392	2000
n-Hexane	—	—	222	8200	—	—	300	10300
Water (pH=3)	—	—	226	6800	—	—	318	10000
Water (pH=9.4)	—	—	228	6000	(260)	(1000)	400	18300

mark. Approximate values are given in parentheses. The values of λ and ε are given e band maximum.

In alkaline solutions all the bands in the spectra of three isomers experience a bathochromic shift, the band being the one experiencing the largest shift. The moval of a proton from the hydroxy group did not nge the number of bands in the spectra of the ortho- l meta-nitrophenols. In the spectrum of para-nitro- nol a weak band (inflection), assigned by us to the C- d, occurs between the B- and D-bands.

The spectra of undissociated molecules of ortho- and ta-nitrophenols contain 4 bands A, B, C, and D, of ch the short-wavelength A-band occurs at the limit of quartz ultraviolet range and is clearly apparent only alkaline solutions. It can be assumed that in the para- rophenol spectrum this band occurs at λ < 200 mμ as

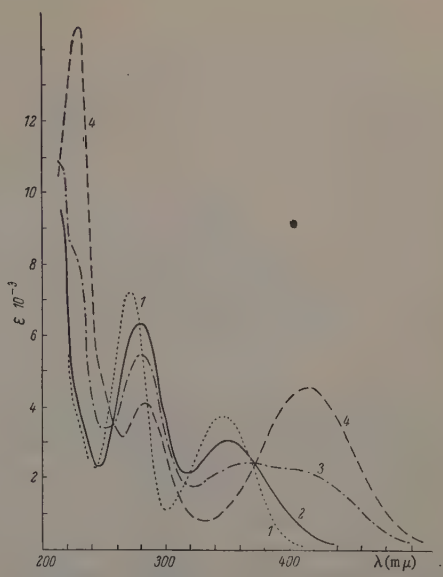

Fig. 5. The absorption spectra of solutions of o-nitrophenol in n-hexane (curve 1) and water (curves 2-4). pH values: curve 2—5.9; curve 3—7.3; curve 4—11.9.

was shown[2] in the case of other para-substituted benzene derivatives. Thus there is one less band in the para-nitrophenol spectrum than in the spectra of ortho- and meta-nitrophenols. This difference between the spectra of the ortho- and meta-isomers on one hand and the para-isomer spectrum on the other, is observed in the spectra of other disubstituted benzenes where the two substituents exert opposing orienting effects, e.g., ref. 6, and is apparently a specific peculiarity of compounds of this type.

CONCLUSIONS

1. The A-, B-, and C-bands of benzene are present, though somewhat shifted, in the spectra of the simplest

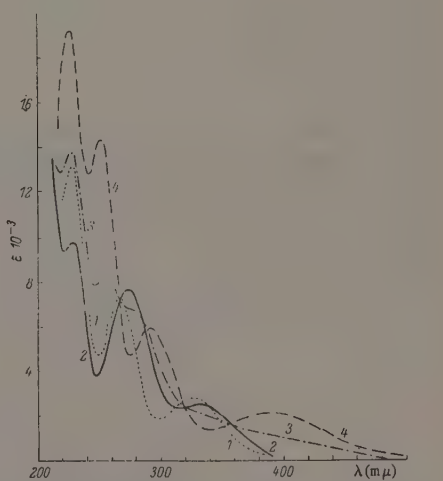

Fig. 6. The absorption spectra of solutions of m-nitrophenol in n-hexane (curve 1) and water (curves 2-4). pH values: curve 2—6.5; curve 3—8.4; curve 4—water + 0.05N NaOH.

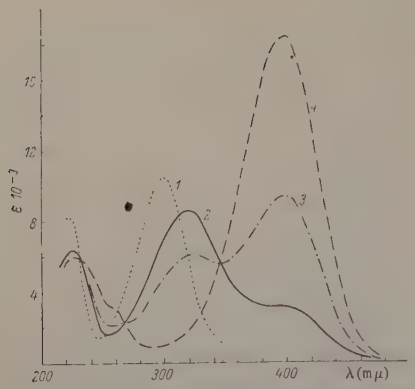

Fig. 7. The absorption spectra of solutions of p-nitrophenol in n-hexane (curve 1) and water (curves 2-4). pH values: curve 2—6.5; curve 3—7.5; curve 4—9.4.

monosubstituted benzenes, the A-band is always in the region $\lambda < 200$ mμ. If the substituent is a group containing an unshared electron pair (e.g. NO_2), then an additional weak D-band is observed on the long-wavelength side. This band has no analogue in the benzene spectrum and belongs to the n—π transition.

2. The spectra of all three isomers of the disubsti tuted benzenes containing substituents exerting similar orienting effects are similar with respect to the numbe of bands and different with respect to the intensities an positions of bands. The bands are modified A-, B-, and C-bands of benzene. At the same time, just as in the monosubstituted benzenes, the A-band lies below 200 m If the substituent contains an unshared electron pair or if ortho- and para-quinoid structures (e.g. in dihydroxy benzenes) can occur then a weak D-band exists at long wavelengths.

3. The spectra of isomeric disubstituted benzenes containing substituents exerting opposing orienting effects differ one from the other. A-, B-, C-, and D-band are present in the spectra of the ortho- and meta-isomers and only three bands in the para-isomer spectrum The A-band in the spectra of the ortho- and meta-isomers is at the edge of the quartz ultraviolet region and occurs rarely in the region $\lambda > 200$ mμ (e.g., in alkalin solutions of nitrophenol). It is assumed that in the para isomer spectrum this band occurs in the region $\lambda < 20$ mμ and hence the band occurring first on the short wavelength side must be identified as the B-band. The D-ba in the spectra of these compounds becomes intense and loses the properties of an n—π transition.

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ON THE THEORY OF LINE WIDTHS IN VIBRATIONAL AND RAMAN SPECTRA OF MOLECULES IN DIPOLE LIQUIDS

K. A. Valiev (pp. 465-470)

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The line width in vibrational spectra of molecules in dipole liquids is calculated for processes which dissipate or exchange the molecular vibrational energy and which arise from the dipole interactions of the molecules. It is shown that the calculated values of the line widths are somewhat smaller than observed values.

RODUCTION

A detailed theory of line widths and shapes in vi- tional and Raman spectra of liquids does not exist e present time.

In investigations by Buchheim[1] and Vol'kenshtein[2] es- tes of the displacement and width of the Raman lines quids were made. These authors considered the ef- of the intermolecular electric forces on Raman lines peculiar type of statistical Stark effect. According e calculations of Vol'kenshtein[2] the electric forces dipole liquid are capable of producing displacements broadening of Raman lines agreeing in order of mag- te with those observed (~1%). Sobel'man[3] calculated idth of vibrational lines of molecules in gases due e unresolved rotational structure of the vibrational sition, but gave only a qualitative treatment of the of the molecular rotation in the broadening of vibra- al lines of liquids. Experimental data on the width shape of vibrational lines in liquids are also meager; is evidently partly due to the lack of a theory which nt explain the nature and significance of these char- ristics of the observed lines. For this reason the ng up of a detailed theory of the width of Raman offers a good deal of interest.

There can be various agencies responsible for the dening of vibrational lines in liquids. In the present stigation a calculation is carried out for the broad- g of vibrational lines in dipole liquids where the dening is assumed to originate in processes in h vibrational energy of molecules is dissipated or anged. These processes are possible because of the trical interactions of the dipole molecules. A num- of other causes of broadening of vibrational lines re- d to the perturbation of the vibrational energy levels, n as anharmonicity, rotation-vibrational interaction, Doppler effect, have been discussed in a paper by dsberg.[4] In the following we assume that in the di- liquid in question there is no hydrogen bonding, e when hydrogen bonding is present the role of the ecular electric moment is of minor importance.[5]

ERGY OF INTERACTION OF MOLECULAR VIBRATIONS WITH THE ENVIRONMENT IN A DIPOLE LIQUID

Let us consider a given molecule in the liquid. Its rgy in the electric field of the surrounding particles be represented as the series expansion[6]

$$H = q\varphi - \mathbf{d}\cdot\operatorname{grad}\varphi + \frac{1}{6}\,\mathbf{D}_{\alpha\beta}\cdot\frac{\partial^2\varphi}{\partial x_\alpha\cdot\partial x_\beta} + \ldots, \qquad (1)$$

where q, $\mathbf{d}$, $\mathbf{D}_{\alpha\beta}$ are the charge, the dipole, and the quadrupole moment of the molecule, and φ, $\operatorname{grad}\varphi$, and $\partial^2\varphi/\partial x_\alpha\cdot\partial x_\beta$ are respectively the potential, the intensity, and the gradient of the intensity of the electric field of the particles surrounding the molecule. For neutral dipole molecules it is sufficient to consider only the second term of the expansion; if the dipole moment is zero the molecular quadrupole moment must be taken into account.

We shall number the dipole molecules of the surroundings with the index A. Then

$$H_{\text{dip}} = \sum_A R_A^{-5}\left[\mathbf{d}\cdot\mathbf{d}_A\cdot R_A^2 - 3\,(\mathbf{d}_A\cdot\mathbf{R}_A)(\mathbf{d}\cdot\mathbf{R}_A)\right]. \qquad (2)$$

We shall describe the internal vibrations of the molecule by a set of normal coordinates Q_i and expand the dipole moment of the molecule as a series in the coordinates Q_i, retaining only the linear terms of the expansion,

$$\left.\begin{aligned} \mathbf{d} = \mathbf{d}_0 + \sum Q_i\mathbf{D}_i, \quad \mathbf{d}_A = \mathbf{d}_A^0 + \sum_i Q_{iA}\mathbf{D}_{iA}, \\ \mathbf{D}_i = \frac{\partial\mathbf{d}}{\partial Q_i}\,. \end{aligned}\right\} \qquad (3)$$

Then the part of (2) which depends on the coordinates Q_i has the form

$$H' = H_1' + H_2',$$

$$H_1' = \sum_i Q_i \sum_A R_A^{-5}\left[R_A^2(\mathbf{d}_A\cdot\mathbf{D}_i) - 3\,(\mathbf{d}_A\cdot\mathbf{R}_A)(\mathbf{d}\cdot\mathbf{R}_A)\right], \qquad (4a)$$

$$H_2' = \sum_{i,\,i_A,\,A} Q_i\cdot Q_{iA}\cdot R_A^{-5}\left[R_A^2(\mathbf{D}_{Ai}\cdot\mathbf{D}_i) - 3\,(\mathbf{D}_{Ai}\cdot R_A)(\mathbf{D}_i\cdot R_A)\right]. \qquad (4b)$$

The expressions under the summation sign $\sum_A$ in (4) suggests the energy of dipole interaction and can be expanded in a series of spherical harmonics[7]

$$V_A = R_A^{-3}d_A D_i\,(A + B + C + D + E + F), \qquad (5)$$

where

$$\left.\begin{aligned} A &= -\frac{8\pi}{3}\sqrt{\frac{4\pi}{5}}\,Y_1^0\ (\alpha,\beta)\,Y_1^0(\alpha_A,\beta_A)\,Y_2^0(\theta_A,\varphi_A), \\ D &= -\frac{8\pi}{3}\sqrt{\frac{3\pi}{5}}\left[Y_1^{-1}(\alpha,\beta)\,Y_1^0(\alpha_A,\beta_A)\right. \\ &\quad \left. + Y_1^0(\alpha,\beta)\,Y_1^{-1}(\alpha_A,\beta_A)\right]Y_2^1(\theta_A,\varphi_A), \\ B &= \frac{8\pi}{3}\sqrt{\frac{\pi}{5}}\left[Y_1^{-1}(\alpha,\beta)\,Y_1^1(\alpha_A,\beta_A)\right. \\ &\quad \left. + Y_1^1(\alpha,\beta)\,Y_1^{-1}(\alpha_A,\beta_A)\right]Y_2^0(\theta_A,\varphi_A), \\ E &= \frac{8\pi}{3}\sqrt{\frac{6\pi}{5}}\left[Y_1^1(\alpha,\beta)\,Y_1^1(\alpha_A,\beta_A)\right]Y_2^{-2}(\theta_A,\varphi_A), \end{aligned}\right\}$$

$$C = \frac{8\pi}{3}\sqrt{\frac{3\pi}{5}}\left[Y_1^0(\alpha,\beta)\,Y_1^1(\alpha_A,\beta_A) + Y_1^1(\alpha,\beta)\,Y_1^0(\alpha_A,\beta_A)\right]Y_2^{-1}(\theta_A,\varphi_A),$$
$$F = \frac{8\pi}{3}\sqrt{\frac{6\pi}{5}}\left[Y_1^{-1}(\alpha,\beta)\,Y_1^{-1}(\alpha_A,\beta_A)\right]Y_2^2(\theta_A,\varphi_A). \qquad (6)$$

The expressions (5) are convenient for taking averages. Here α, β, α_A, β_A, θ_A, φ_A are the spherical angle coordinates specifying the orientation (in the laboratory coordinate system), respectively, of the vector $\mathbf{D}_i$ of the given molecule, the moment $\mathbf{d}_A$ of the molecule A, and the radius vector $\mathbf{R}_A$ drawn from the given molecule to the molecule A.

The energy (4) must be considered classically as the potential of the electrical dissipative forces acting on the vibration of the molecule. From the quantum mechanical point of view the perturbation (4), which is time dependent, can cause transitions between the energy levels of the oscillator Q_i with transfer of energy from the oscillator to the thermal motion (dissipation) or to the other oscillators of the system (exchange). We shall now deal with the calculation of the probabilities of these processes.

PROBABILITY OF PROCESSES OF DISSIPATION OF THE MOLECULAR VIBRATIONAL ENERGY

The first term in (4) represents the energy of the vibrations Q_i of the given molecule in the time-dependent electric field of the surrounding particles. Under the influence of this field the oscillator Q_i performs transitions, the probabilities of which can be calculated by the perturbation theory formula

$$W_{n_i-1\to n_i} = \hbar^{-2}\langle|H'_{n_i-1\to n_i}|^2\rangle j(\omega_{n_i-1\to n_i}). \qquad (7)$$

Here n_i, ω_i are the quantum number and the frequency of the oscillator Q_i; the angle brackets indicate the average over the variables of H'; $j(\omega)$ is the spectral density of the perturbation corresponding to the frequency ω.

In calculating the spectral density $j(\omega)$ from the function $H'(t)$ randomness can be assumed since the time dependence of H' is due to random processes, namely, the rotational and translational diffusion of the particles. For simplicity we will consider the rotation and the translational motion of the particles as independent motions and their respective contributions to the vibrational relaxation as additive. The spectral density $j(\omega)$ of any random function $f(t)$ can be given in terms of the correlation function $g(\tau)$ normalized to the values $g(0) = 1$ and $g(\infty) = 0$.[8]

$$j(\omega) = \int_{-\infty}^{+\infty}\exp(-i\omega\tau)\,g(\tau)\,d\tau, \qquad (8)$$

$$g(\tau) = \frac{\langle f^*(t+\tau)\,f(t)\rangle}{\langle|f(t)|^2\rangle}. \qquad (9)$$

For the quantities which fluctuate in the process of rotational diffusion, $g(\tau)$ and $j(\omega)$ have the forms

$$g(\tau) = \exp\left[-\frac{l(l+1)\,D_r\tau}{a^2}\right] = \exp\left[\frac{-\tau}{\tau_r}\right], \qquad (10)$$

$$j(\omega) = \frac{2\tau_r}{1+\omega^2\tau_r^2}. \qquad (11)$$

Here $D_r = kT/8\pi\eta a$ is the coefficient of rotational diffusion; a is the Stokes radius of the molecule; l is the order of the spherical harmonic which changes during the rotation of the particles.

The functions $Y_1^m(\alpha,\beta)$ and $Y_1^m(\alpha_A,\beta_A)$ in (5) change during the molecular rotation. We will assume that the molecules rotate independently of one another so that the functions $Y_1^m(\alpha,\beta)$ and $Y_1^m(\alpha_A,\beta_A)$ are independent random functions. Thus the correlation function $g(\tau)$ of the product $Y_1^m(\alpha,\beta)Y_1^m(\alpha_A,\beta_A)$ is equal to the product $g_1(\tau)g_2(\tau)$ of the correlation functions of $Y_1^m(\alpha,\beta)$ and $Y_1^m(\alpha_A,\beta_A)$, that is,

$$g(\tau) = \exp\left[\frac{-\tau}{\tau_{r1}}\right]\exp\left[\frac{-\tau}{\tau_{r2}}\right].$$

If all the molecules in the liquid are identical, then $\tau_{r1} = \tau_{r2} = 4\pi\eta a^3/kT = 4\tau_0$ and

$$j_r(\omega) = \frac{8\tau_0}{1+16\omega^2\tau_0^2}.$$

The correlation function $g(p) = g(\tau/\tau_t)$ of the energy of the dipole interaction perturbed by the translational diffusion of the particles was calculated in our earlier paper[9]:

$$g_t(p) = \frac{3}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{3}\Phi\left(\frac{1}{\sqrt{p}}\right) + \frac{1}{3}p^{1/2}e^{-1/p} - p^{1/2} + \frac{2}{3}p^{3/2}(1-e^{-1/p})\right],$$

where $\Phi(x)$ is the error integral, and the spectral density corresponding to (14) is

$$j_t(\omega) = 3\tau_t\left[(Z^{-3}-2Z^{-5}) + e^{-Z}\cos Z\,(Z^{-3}+4Z^{-4}+2Z^{-5}) + e^{-Z}\sin Z\,(Z^{-3}-2Z^{-5})\right],$$
$$Z = \sqrt{2\omega\tau_t},\quad \tau_t = \frac{2a^2}{D_t} = 12\,\frac{\pi\eta a^3}{kT} = 12\tau_0. \qquad (15)$$

It is easy to find limiting expressions for (15):

$$j_t(\omega) = \frac{3}{4\sqrt{6}\,\omega^{3/2}\tau_0^{1/2}} \quad \text{for } \omega\tau_0 \gg 1,$$

$$j_t(\omega) = \frac{24}{5\tau_0} \quad \text{for } \omega\tau_0 \ll 1.$$

We will now derive the value of $\langle|H^1_{n_i-1\to n_i}|^2\rangle$. The matrix element of the transition $n_i - 1 \to n_i$ is equal to

$$H'_{n_i-1\to n_i} = D_t\left(\frac{n_i\hbar}{2m_i\omega_i}\right)^{1/2}\sum_A R_A^{-3}d_A V_A.$$

After averaging the square of (18) over the angles and the volume we obtain

$$\left\langle\left|H'_{n_i-1\to n_i}\right|^2\right\rangle = \frac{Nn_i\hbar}{2m_i\omega_i}\cdot\frac{8\pi}{9}\cdot\frac{d^2D_i^2}{(2a)^3},$$

where N is the number of molecules in 1 cm^3. Finally in accordance with (7), (13), (16), and (19) we write down the expression for the probability of the transition $n_i \doteq 1 \to n_i$ for $\omega\tau_0 \gg 1$:

$$W_{n_i-1\to n_i} = \frac{8\pi}{9}\cdot\frac{Nn_i\cdot\hbar^{-1}}{2m_i\omega_i}\cdot\frac{d^2D_i^2}{(2a)^3}\cdot\left[\frac{1}{2\omega_i^2\tau_0} + \frac{\sqrt{3}}{4\omega_i^{3/2}\tau_0^{1/2}}\right].$$

Let us consider formula (20). If the width of the vibrational line is determined by the dissipative process in question, the width of the line and its intensity should change in a parallel way. High frequency lines should be narrower: the width decreases with increasing frequency approximately as $\omega^{-5/2}$. An appreciable temperature dependence of the width should be observed; this is due to the temperature variation of $\tau_0 = \pi\eta a^3/kT$. If we take into account that $(\omega_i/\tau_0)^{1/2} > \tau_0$, we obtain

$$W_{n_i-1\to n_i}\sim\sqrt{\frac{T}{\eta}}. \qquad (21)$$

is, the line should broaden as the temperature of the uid is raised.

We will make a numerical estimate of the band width means of formula (20), selecting the following values the quantities: $N_i = 3\times10^{22}$; $n_i = 1$; d = 1D; 2a = 4 A; $= 2\times10^{-24}$ gm; $D_i = 5\times10^{-10}$ cgs units;[2] $\tau_0 = 3\times10^{-12}$; $\omega_i = 5\times10^{14}$ sec^{-1}. Then, $W_{n_i-1\to n_i} = 4\times10^9$ sec^{-1}. If $= 10^{14}$ sec^{-1}, $W_{n_i-1\to n_i} = 5\times11$ sec^{-1} = 2.5 cm^{-1}.

CHANGE OF QUANTA BETWEEN MOLECULES

The quantity (4b) represents the energy of interac- of the vibrations Q_i and Q_{iA} of two different mole- s arising from the electric forces. Because of this raction the molecules can exchange quanta of vibra- al energy. If Q_i and Q_{iA} are the coordinates of iden- l vibrations of the two molecules, possessing the e frequency ω_1, then, because of the interaction (4b) vibrations Q_i and Q_{iA} can exchange quanta directly out the participation of a third degree of freedom of system. Such an exchange can be called a resonant hange. Also a nonresonant exchange of quanta be- en vibrations of different frequencies is possible; the erence in energy of the quanta can be passed over to thermal motion of the liquid, which has a continuous rgy spectrum and is represented in (4b) by the spa- coordinates of the particles.

We will calculate the probability of the resonant ex- nge. The matrix element of this type of transition is al to

$$H'(n_i-1,\ n_{iA}\to n_i,\ n_{iA}-1) = \frac{\hbar D_i}{m_i\omega_i}\cdot\sqrt{\frac{n_i}{4}}\sum R_A^{-3}\cdot D_{iA}\sqrt{n_{iA}}\,\Omega_A. \qquad (22)$$

is used to designate the sum of the quantities (6). raging of the square (22) is entirely similar to that ried out above, that is,

$$\langle|H'|^2\rangle = \frac{\hbar^2 n_i n_{iA}}{4m_i^2\omega_i^2}\cdot\frac{8\pi}{9}\cdot\frac{ND_i^2D_{iA}^2}{(2a)^3}. \qquad (23)$$

The probability (frequency) of the exchange can now evaluated from the formula

$$W_{res.} = \hbar^{-1}[\langle|H'|^2\rangle]^{1/2} = \frac{1}{3}\frac{D_iD_{iA}}{m_i\omega_i}\left[\frac{2\pi N n_i n_{iA}}{(2a)^3}\right]^{1/2}. \qquad (24)$$

Since in the phenomenon in question (vibrational ctra) only the zero and first vibrational states of the lecule take part, one can put $n_i = n_{iA} = 1$ in (24). More- r, in numerical evaluations of the exchange probabil- the quantum-mechanical probability (24) must be ltiplied by the statistical probability, $W_{stat.}$, that one he two vibrations (Q_i or Q_{iA}) possesses a vibrational ntum $\hbar\omega_i$ (that is, is found in the level with quantum nber $n_i = 1$).

Values of $W_{res.}$, calculated from (24) for high-fre- ncy vibrations ($\omega_i = 10^{14}$ sec^{-1}) are too small (chiefly ause of the smallness of the statistical factor, $W_{stat.} = ^{-4}$-10^{-8}) to explain observed line widths. However, in case of low-frequency vibrations the resonant ex- nge of quanta can make an appreciable contribution he line width. For T = 300° and $\omega_i = 500$ cm^{-1}, $W_{stat.} = 0.1$. If we assume in addition, $m_i = 2\times10^{-23}$, $D_i = 5\times10^{-10}$, $N = 3\times10^{22}$, 2a = 3 A, then $W_{res.} = 2\times10^{11}$ sec^{-1} = 1.0 cm^{-1}.

We note that the magnitude of $W_{res.}$ determines the velocity of migration (diffusion) of vibrational quanta in the substance. It is easy to find the linear velocity of migration of quanta from the general formulas of diffusion theory, if we consider the displacement of the quantum in one transition to be equal to the diameter of the molecule, 2a, and the lifetime of the quantum in a given molecule equal to $W_{res.}^{-1}$.

Formula (24) can obviously be used to evaluate the frequency of exchange of quanta between degenerate vibrations of one and the same molecule. For example, in the linear molecule $XY_2(CO_2)$ the vibrations perpendicular to the axis of the molecule are doubly degenerate, and both perpendicular vibrations generate dipole moments. The energy of interaction of these dipoles is given by (4b); the effective distance 2a between the two dipoles can be considered negligible.

Our calculations show that the probabilities of processes of nonresonant exchange of quanta reach a value of about 10^{10} sec^{-1} only in favorable cases (low-frequency vibrations, near equality of the vibrational frequencies). We have also carried out the calculation of the probability of the process of energy dissipation for infrared inactive vibrations (not producing a change in the dipole moment of the molecule). The probability of these processes is of the order of 10^8 sec^{-1}.

CONCLUSION

The broadening of lines of infrared active vibrations of molecules, produced by processes involving dissipation and resonant exchange of vibrational energy, agrees in order of magnitude with, but is smaller than, the observed widths. The variation of the broadening with increasing temperature of the liquid, as predicted by formulas (20) and (24), agrees with existing observations. Lines whose widths are determined by dissipative processes will have a dispersion shape. The effect of dissipative processes on the line widths of infrared-inactive vibrations is shown by our calculations to be negligibly small.

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CALCULATION OF THE FREQUENCIES AND INTENSITIES OF THE INFRARED SPECTRUM OF PROPENYL BROMIDE

M. P. Leontovskii (pp. 471-477)

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The infrared spectrum of the cis- and trans-isomers of propenyl bromide with cis- and trans-orientations of the methyl group (4 variants) has been computed. The observed frequencies are assigned to the normal vibrations. The rule for distinguishing cis- and trans-isomers is generalized.

1. Diagram of the Molecule. The structure of the molecule of the cis-isomer of propenyl bromide is shown in Fig. 1 with a designation of the internal coordinates and the accepted bond lengths. The trans-isomer differs by the appropriate change in the directions of the $C_2—H_2$ and $C_2—Br$ bonds. The two hydrogen atoms of the methyl group which merge into a single point when the diagram is projected are denoted by H_6 and H_7 (H_6 is considered to be located above the plane of the diagram and H_7 below it). The calculations were carried out both for the orientation shown in the figure, where the atom H_5 is located in the transposition relative to H_1, and for the cis-position relative to H_1, i.e., when the atoms H_5, H_6, and H_7 are reflected in the zx plane.

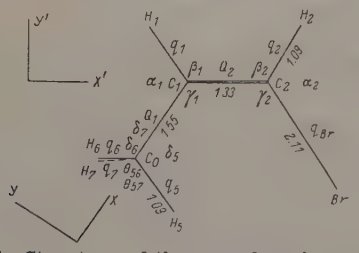

Fig. 1. Structure of the propylene bromide molecule.

The following coordinates are not shown in the figure: ρ_1—the angle of the $C_1=C_2$ bond with the $C_0C_1H_1$ plane; ρ_2—the same for the BrC_2H_2 plane; χ—the relative rotation of these planes around the C=C axis. The methyl group angles at the atom C_0 are taken as tetrahedral, and the remaining angles as equal to 120°.

2. Force Constants (Table 1). The known constants of ethane[1] and ethylene[2]* are the basis for the calculation. The constant for the $C_2—Br$ bond was computed according to Badger's formula.[3] We ignore the torsional constant of the methyl group around the $C_0—C_1$ bond, and we omit this coordinate.

*Rounded-off values.

Table 1

Diagonal	Stretching	Q_2	+14.2	Ethylen
		Q_1	+ 7.02	Ethane
		q_1, q_2	+ 8.6	Ethylen
		q_5, q_6, q_7	+ 8.08	Ethane
		q_{Br}	+ 3.07	Badger's formul
	Angular	α_1, α_2, β_1, β_2, γ_1, γ_2, θ_{56}, θ_{57}, θ_{67}	+ 0.70	Ethane ethyle
		δ_5, δ_6, δ_7	+ 0.92	Ethane
		ρ	+ 0.32	Ethylen
		χ	+ 0.76	Ethylen
Nondiagonal	Sides with a common vertex		+ 0.07	Ethane, ethyle
	Side and its angle		+ 0.43	Ethane, ethyle
	Angles with a common side, in the methyl group only		− 0.04	Ethane
	ρ_1, ρ_2		+ 0.05	Ethylen
	cis-$\gamma_1\beta_2$, $\gamma_2\beta_1$		+ 0.1	Ethylen
	trans-$\gamma_1\gamma_2$, $\beta_1\beta_2$		+ 0.1	Ethylen

Note: Force constants are in units of 10^6 cm^{-2}.

3. Derivatives of the Dipole Moment of the Molecule, μ. We write the derivatives of μ_x, μ_y, and μ_z with respect to displacements of the atom A in the directions ξ, η, ζ in the form

$$\frac{\partial \mu_x}{\partial \eta_A} = \varepsilon_{x\eta} \cos x\eta \qquad (1)$$

(and so on, 9 formulas).

Not knowing the exact quantities, we assume as an approximation, according to the averaged data from re 4 and 5, that all the ε values for the H atoms equal ±0.40 D/A (except for $\varepsilon_{x\eta} = +0.20$ D/A for the methyl group). For the bromine, we average the data from re 6. The ε values (in D/A) taken as a basis for the calcu lation are presented in Table 2.

Table 2

$H_{ethylene}$				H_{methyl}				Br			
	ξ	η	ζ		ξ	η	ζ		ξ	η	
x'	−0.40	−0.40	—	x	−0.40	+0.20	—	x'	−1.80	−0.74	
y'	−0.40	+0.40	—	y	−0.40	+0.40	+0.40	y'	−1.80	−0.74	
z'	—	—	+0.40	z	−0.40	+0.40	+0.40	z'	—	—	

Here x, y, z and x', y', z' are Cartesian coordinates (see Fig. 1), and ξ is in the bond direction. In th ethylenic portion, η lies in the plane of the molecule, while in the methyl group it lies in the HC_0C_1 plane ($\xi \perp \eta \perp \zeta$). In the empty spaces, there are no values of ε on account of symmetry considerations. We emphasize that the derivatives of a moment with respect to displacements of the carbons are functions of ε for the h drogens and the bromine (see Appendix).

4. Results of the Calculations. The results obtain are presented in Tables 3 and 4 and in Figs. 2 and 3. frequency and intensity values for the reflected methyl group came out practically the same, and are therefor

Table 3. trans-Propenyl Bromide

Theory				Experiment	
Relative intensity		Characteristics of the vibration	Symmetry	Frequency (cm^{-1})	Relative intensity
27		eth.	pl.		
1.0		eth.	pl.		
13	55	str., H meth.	npl.	2950	55
11		meth.	pl.		
3.5		meth.	pl.		
3.6		C=C	pl.	(1655)	3.6
				1625	9.5
				(1575)	2.2
6.5	14	def., $H_{meth.}$	npl.		
7.0		def., H_{meth}	pl.	1440	16
7.6		def., $H_{meth.}$ (symmetric)	pl.	1380	5.2
0.0		def., $H_{eth.}$ (to different sides)	pl.	1300	13
29		def., $H_{eth.}$ (to same side)	pl.	1220	18
1.0		"C_0–C_1" complex	pl.	1100	1.3
1.6		def., H except H_2	npl.	1050	1.3
24	28	def., $H_{eth.}$ (twisting C=C)	npl.		
3.9		Complex def., $H_{meth.}$ + "C_0–C_1"	pl.	935	35
2.9		def., $H_{eth.}$ (not twisting C=C)	npl.	720	6?
1.3		"C_2–Br"	pl.		
3.0		Change in length of molecule	pl.		
0.0		Bending of molecule	npl.		
0.0		Bending of molecule	pl.		
?		Rotation of methyl group around C–C	npl.		

Symbols: str. – stretching, def. – deformation, pl. – planar, npl. – nonplanar vibrations. Unidentified frequencies are shown in parentheses.

Table 4. cis-Propenyl Bromide

Theory				Experiment	
Relative intensity		Characteristics of the vibration	Symmetry	Frequency (cm^{-1})	Relative intensity
21		eth.	pl.		
69		eth.	pl.		
13	55	str., H meth.	npl.	2950	55
11		meth.	pl.		
3.2		meth.	pl.		
1.6		C=C		1625	16
				(1580)	6.5
6.6	14	def., $H_{meth.}$	npl.	1450	19
7.0		def., $H_{meth.}$	pl.		
7.7		def., $H_{meth.}$ (symmetric)	pl.	1390	11
24		def., $H_{eth.}$	pl.	1305	32
5.1		def., $H_{eth.}$	pl.	1215	6.1
6.5		"C_0–C_1" (complex)	pl.	1040	2.6
3.5		def., $H_{eth.}$ + meth.	npl.		
1.9	5.2	def., $H_{eth.}$ (twisting C=C)	npl.	935	18
3.3		Complex def. $H_{meth.}$ + "C_0–C_1"	pl.		
20		def., $H_{eth.}$ (not twisting C=C)	npl.	700	?
9.0		"C_2–Br"	pl.	—	—
3.8		Change in length of molecule	pl.	—	—
2.4		Bending of molecule	npl.	—	—
1.2		Bending of molecule like a tuning fork	pl.	—	—
?		Rotation of methyl group arounc C–C	npl.	—	—

Note: For symbols, see note to Table 3.

given (for the method of calculation, see Appendix).

5. Spectra. We used 2 spectra of the trans-isomer propenyl bromide and 1 spectrum of the cis-isomer, ained by Chumaevskii by means of a double-beam ctrometer.[7]

The spectra were replotted on a linear frequency le and a logarithmic ordinate scale. In view of the all scale of the originals and the difficulties in the narcation of merging adjacent bands, the errors in estimates of the integrated intensities may in isolated es reach 30-40%.

6. Comparison of Experimental and Calculated Data. tching of the calculated results with experiment has de it possible to identify the bands with confidence. e experimental frequency values are written out op-

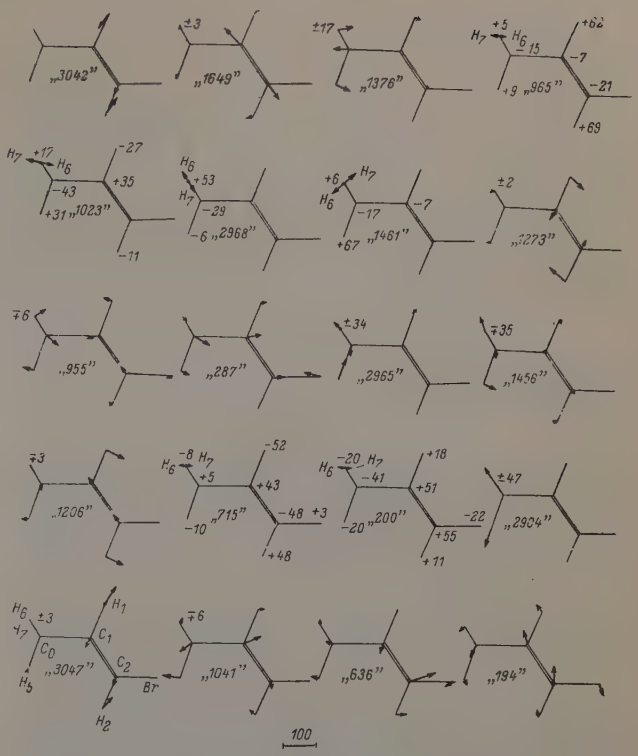

Fig. 2. Normal vibrations of trans-propenyl bromide. Arrows show the directions of the weighted atomic displacements (i.e., $\times\sqrt{m}$). Figures near atoms denote weighted displacements along the z-axis, directed upward. For the atoms H_6 and H_7, the upper sign on the figure refers to H_6 (H_6 is above the plane of the diagram, H_7 below it). Numbers are frequencies in cm^{-1}.

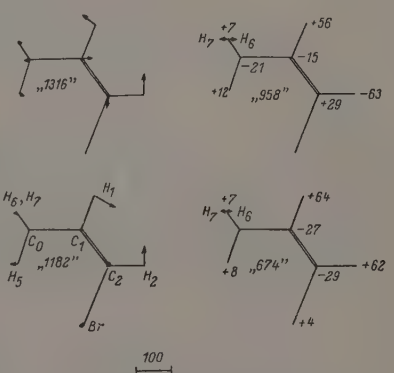

Fig. 3. Normal vibrations of cis-propenyl bromide. For symbols, see legend to Fig. 2.

posite the corresponding theoretical ones (Tables 3 and 4). Experimental frequency values which are probably combinations are shown in parentheses. The identification presented agrees well with the literature data.[8]

In the experimentally obtained spectrum, the bands of 5 C–H stretching vibrations merge, as well as the frequencies 1461 and 1456 and 965 and 955 of the trans-isomer, and 958 and 935 of the cis-isomer. The theoretical frequency values are close to the experimental ones,

in consequence of which there was no necessity for "fitting" the theory to experiment by changing the force constants.

The theoretical intensity values also agree qualitatively with the experimental ones. Only the theoretical estimates for the deformation vibrations of the hydrogens of the ethylene group when they vibrate in opposite phase (in the trans-isomer) and for the C=C vibration are substantially too low. This comes about because the moment derivatives which we have accepted do not take account of the pronounced asymmetry of the C=C brought about by the halogen.

7. Comparison of the Spectra of the cis- and trans-Isomers. We have 4 normal vibrations of the ethylenic hydrogens (Table 5).

Table 5

cis-		Characteristics of the vibration	trans-	
i	1316	Planar C=C turning	1273	w
w	1182	Planar C=C nonturning (the C=C direction does not change during the vibration)	1206	i
w	958	Nonplanar C=C twisting (the coordinate χ changes greatly)	965	i
i	674	Nonplanar C=C nontwisting (see Figs. 2 and 3)	715	w

Symbols for intensities: i – intense, w – weak. Frequencies are in cm^{-1}.

Since the double bond resists twisting, it is natural that vibrations which twist it must be of higher frequency than nontwisting vibrations. We have found that such a picture exists for four other molecules: cis- and trans-propenyllithium and the cis and trans Biginelli complexes.

When the hydrogen atoms shift in the same direction, the intensity of the bands is high, but in the opposite case it is low. In the trans-isomer, when the hydrogens move in the same direction they twist the C=C bond but do not turn it, and vice versa in the cis-isomer. For just this reason, the intensities of the H bands in the spectrum of the trans-isomer run thus, in order of frequency: || ||, and in the cis-isomer, thus: || ||, as is also shown in Table 5. This rule must be fulfilled for many molecules and has long been known for nonplanar vibrations. It can be seen from Tables 3 and 4 that it is also confirmed for planar vibrations.

The methyl group vibration frequency 955 or 935 cm^{-1} is superimposed on the frequency of ethylenic vibrations which twist the C=C bond in the given molecule (and many similar molecules). The intensity of this band does not change on going from the trans- to the cis-isomer. Therefore, the entire band observed experimentally does not disappear, but is only weakened in the spectrum of the cis-isomer.

APPENDIX. A SIMPLE CALCULATION OF THE INFRARED SPECTRUM

The calculation was carried out in weighted Cartesian coordinates. The B matrix of the transition from internal to weighted coordinates was set up. By means of an electronic computer, the potential energy matrix U $\tilde{B}VB$ was found in weighted coordinates (V is the poten energy in internal coordinates). Furthermore, the uni tary matrix C which diagonalizes U was found:

$$C^{*}UC = \Lambda, \quad C^{*}C = 1,$$

where Λ is the diagonal matrix of the squares of the f quencies, C_{ik} being the weighted coordinate i of the k-th normalized vibration.

The calculation of the intensities was carried out the following way.

The derivatives of the dipole moment of the molec which were given in the single coordinate system x, y, were found according to formula (1) with the help of th assumed ε values (the derivatives with respect to all the hydrogens and the bromine linked by bonds with a carbon atom were summed, the signs were changed, a the values of the derivatives with respect to a displace ment of this carbon were obtained). After division of a the derivatives by $\sqrt{m}$, where m is the mass of the at in question, the K matrix of the derivatives of the dip moment of the molecule with respect to the weighted Cartesian coordinates of the atoms was obtained. The intensity of the absorption bands for one molecule is d termined by the formula

$$I = \frac{\pi}{3c}\tilde{C}\tilde{R}KC$$

(with the exception of the temperature factor).

The derivatives of the frequencies may be comput with the help of the expression

$$d\Lambda = C^{*}(dU)C.$$

In conclusion, I thank A. E. Borisov, N. V. Novikov and N. A. Chumaevskii for furnishing experimental spe tra before publication,[7] and L. S. Mayants, L. A. Kazit yna, and the Computing Center of the Moscow State Un versity for the planning of the work and for valuable su gestions.

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RAMAN LINE INTENSITIES IN THE LIQUID AND GAS PHASE

A. I. Sokolovskaya (pp. 478-481)

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A study of changes in the Raman line intensities of benzene, chloroform, and carbon tetrachloride on the transition from liquid to the gas phase has been carried out. Comparison of the results obtained with the results of theoretical calculations shows that they cannot be explained by the effective internal field theory of Lorentz and Onsager.

In recent years there has appeared a large number tudies in which the authors have attempted to relate bserved changes in the infrared and electronic abtion spectra on transition of the substance from the id to the gas state with the character of the so-called ective" field in the liquids. There exists a whole es of models arising from the polarization theory of id dielectrics with whose help the internal field in the id $E_{eff.}$ is expressed in terms of the field in air E_0. mination of the phenomena observed in the electronic ared absorption spectra, and also Raman scattering, n this point of view, led to the consideration that the rnal dielectric medium surrounding the molecule in liquid does not directly influence the transition probties, but only changes the magnitude of the field of light wave acting on it. Comparison of the spectral nsities in vapors and liquids with results following n the models of Lorentz[1] and Onsager[2] has been car- out in electronic spectra[3] and infrared absorption tra.[4-6]. However, the data obtained are extraordily contradictory. It is necessary to remark that such surements have not been carried out in Raman spec- Since a comparison of the spectral intensities in the and liquid phases represents considerable interest n the point of view of clarifying the character of the rmolecular interactions in liquids it appeared exent to us to carry out such a type of investigation in an spectra. As objects of investigation we chose ids in which any specific intermolecular interactions plex formation, hydrogen bonds, etc.) were excluded. is case one can consider that the intermolecular inctions in the liquids investigated basically appear in r intermolecular dielectric nature. According to the ntz model the observed ratio of the line intensities ne liquid and gas phases will be given by

$$\frac{I_{liq}}{I_{gas}} = \frac{1}{n}\left(\frac{n^2+2}{3}\right)^2, \qquad (1)$$

re n is the refractive index.

We will not examine the formula for the effective ld arising from the Onsager model since its applica- has significance only for solutions, and for pure ids in the absence of an orienting effect it leads to Lorentz equation.[7-9]

In the present work we have studied the change of the intensities of benzene, chloroform, and carbon tetraride on transition of the substance from the liquid to gas phase.

The measurements were carried out photographically V-Sh three-prism spectrograph with a dispersion of mm in the blue region, and 6 A/mm in the violet re- of the spectrum. Low pressure meter lamps served light source. To measure the ratios of the intensities ne liquid and gas phases of the substance we prepared two pyrex cells having an identical operating portion, the length of which was 800 mm and the diameter, 30 mm. The cells were calibrated using the Raman spectrum of liquid benzene. In photographing the spectra the cell was located in a two-lamp illuminator and was treated according to the recommendations of ref. 10. In this case, as we have shown earlier,[11] the apparatus influence of the refractive index appears only through a change of the scattered light flux entering the spectrograph, proportional to the square of the refractive index of the scattering liquid. The vapor and liquid spectra were photographed on high sensitivity fine-grained "Kodak Oa O" plates through a three-step attenuator. The transmission of the attenuator was measured in a preliminary experiment in the operating spectral region of the V-Sh apparatus. The integrated intensity was determined by planimetering the area delineated by the line contour. The integrated intensity of the line of the liquid measured relatively to the integrated intensity of the same line of the vapor, taken equal to 100, was given by

$$I_{liq.} = \frac{I'_{liq.}}{I'_{gas}} I_{gas} \frac{M n^2_{liq.}}{d_{liq.}} \cdot \frac{p}{kT}, \qquad (2)$$

where I_{gas} is the gas intensity for the given temperature, taken equal to 100; $I'_{liq.}$, and I'_{gas} are the observed intensities of the liquid and gas; M is the molecular weight; $n_{liq.}$ and $d_{liq.}$ are the refractive index and density of the liquid at the given temperature; k is the Boltzmann constant; p is the gas pressure; T is the absolute temperature.

Due to the large differences of substance density in the liquid and gas the intensities of the same line in the different phases could not be directly compared. The intensity of the 992 cm^{-1} Stokes line of benzene in the gas phase was compared with the intensity of the 607 Stokes line and the 992 cm^{-1} anti-Stokes line in the liquid. Since the relative line intensities in the spectrum of liquid benzene had been determined earlier by us it was not difficult to find the ratio of the intensities of the 992 cm^{-1} Stokes line in the gas and liquid. In an analogous manner we compared the intensities of the 336 cm^{-1} and 665 cm^{-1} lines in the two phases for chloroform. The mean uncertainty of the measurement of the integrated intensities was approximately 7 to 8% for benzene and chloroform, and somewhat greater (approximately 20%) for carbon tetrachloride. The latter is due to the fact that in the calculation of the ratio of the 459 cm^{-1} line intensity of CCl_4 in the liquid and gas we were forced to use an intermediate standard—chloroform in our case. The Raman line intensities in the gases were measured at +120°C and the liquids at +60°C.

The results of the measurements are given in Table 1. As may be seen from the table the Raman line

Table 1

Substance	$\Delta\nu$ (cm^{-1})	t(°C)	$I_{exp.}$
C_6H_6 . . .	992	+60	240
$CHCl_3$	336	+60	140
	665	+60	140
CCl_4	459	+60	210

Note: The intensity of the gas at +120°C is taken equal to 100.

Table 2

Substance	$\Delta\nu$ (cm^{-1})	t(°C)	$I_{exp.}$	$I_{theor.}$
C_6H_6	992	+ 20	290	136
		+120	140	129
$CHCl_3$	366	+ 20	210	129
		+120	120	125
	665	+ 20	150	129
		+120	124	125
CCl_4	459	+ 20	260	132
		+120	160	126

Note: The intensity of the gas at +20°C and +120°C is taken equal to 100.

intensity in the liquid at 60°C exceeds the line intensity of the gas at 120°C for all of the substances investigated. However, it would be more correct to compare the line intensities in the different phases of a substance for identical temperatures. The latter circumstance, as a rule, has not been taken into account in the studies of the electronic and infrared absorption spectra in gases and liquids. This is possibly valid for complex molecules whose spectral intensities, as has been shown for electronic absorption[3] and Raman scattering,[12] change little with temperature. However, in the case of simple molecules of the carbon disulfide or benzene type[13] failure to account for the temperature dependence of the line intensities in the liquid can lead to incorrect conclusions. To obtain data for identical temperatures in the different phases of a substance we made use of results of extrapolation of the experimental curves of the temperature dependence of the line intensity in the gases and liquids. The relative changes of the line intensities with temperature in these two phases for chloroform, benzene and carbon tetrachloride were carried out by us earlier.[14] It is necessary to note that the temperature changes of the Raman line intensities in the gas phase are not large.[14] Therefore an extrapolation of the temperature dependence of the line intensities in gases over a broad temperature interval can scarcely introduce large errors. The values of the line intensities obtained as a result of the extrapolation are given in Table 2. In the last column of the table are given the line intensities calculated according to formula (1). Since the model considered[1] is approximate to a significant degree, it is not necessary to know accurate values of the refractive index. The value of $n_{liq.}$ used for the calculation of $I_{theor.}$ in Table 2 was obtained by an extrapolation to a temperature of 120°C (superheated liquid).

The changes of the line intensities given in Tables 1 and 2 on transition of the substance from the liquid to the gas state agree in sign with the results obtained taking account of the internal field according to Lorentz. However, significant quantitative deviations are observed. Thus, for example, it is seen from Table 2 that on transition of benzene from the liquid to the gas the line intensity of 992 cm^{-1} for a temperature of 20°C changes approximately three times, and at 120°C about 1.4 times; according to Eq. (1) the intensity of this line at 20°C and 120°C should change approximately 1.3 times. Such a result is not unexpected since the Raman line intensity in the liquid decreases with a temperature increase and these changes cannot be explained within the limits of the model indicated.[1]

According to Lorentz the changes of intensity on transition from the liquid to the gas should be approximately identical for different substances since the variation of the refractive index of the liquid is not great. However, the data of the present study given in Table 2, like the results of ref. 6, contradict this conclusion.

Analysis of the results obtained shows that the ratios found for the Raman line intensities of C_6H_6, CHC and CCl_4 in the liquid and gaseous states cannot be explained from the point of view of the electric field according to Lorentz. In the works of Neporent and Bakhshiev[3,15] molecular parameters (structural radius and polarizability) are introduced into the Onsager formula. Estimates carried out by us have shown that in this case the deviations of our experimental data with the theory increase.

The latter is possibly connected with the incomplete model used to calculate $E_{eff.}$. It is known that Lorentz and also Onsager use a coarse simplified molecular model not taking account of the short range correlation forces and the molecular kinetics in the liquid.[8,16] In the theory of liquid dielectrics there are in existence more complete models in which some of the indicated inadequacies are removed.[8,17] However, the formulas obtained for the magnitude of the effective field in the liquid from these models is quite complex so that they cannot be used for comparison with the experimental results. Evidently, further development of the theory is necessary to explain the observed phenomenon.

In conclusion I express warm thanks to P. A. Bazhulin for his constant interest in the work and for valuable advice.

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RESONANCE SPLITTING OF THE CARBONYL BAND IN THE INFRARED SPECTRUM OF SYDNONES

Yu. G. Borod'ko and Ya. K. Syrkin (pp. 482-485)

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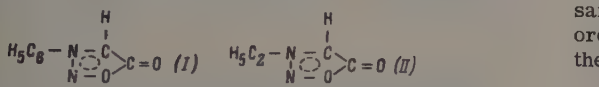
In an earlier communication[1] we mentioned that the bonyl bands in the infrared absorption spectra of 3-nylsydnone (I) and 3-ethylsydnone (II) are double.



We have performed some experiments which show the observed shapes of the bands do not change with centration in the range 10^{-2} to 10^{-4} mole/liter, but depend on the nature of the solvent and the tempera- (Fig. 1). In some solvents (pyridine, chloroform) low-frequency component is more intense, whereas high-frequency one is in others (carbon tetrachloride, achloroethylene). In our opinion, this kind of inten- change cannot be explained on the basis of associa- between the sydnone and solvent molecules, since component intensities do not depend on the concen- ion in the aforementioned range and the splitting is erved in the individual substances. We also note that distance between the carbonyl group oxygen in a none and the hydrogen on the neighboring atom is great (~2.5 A) for an intramolecular hydrogen bond. ides this, the C—H bond in a sydnone molecule is too kly polarized for the hydrogen to participate in a hy- gen bond.

The splitting can evidently be explained by a Fermi onance between the carbonyl level ($\nu_{C=O}$ = 1750 cm^{-1}) an overtone of the vibration of the five-membered

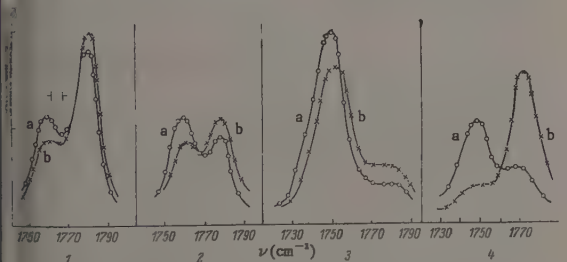


Fig. 1. Observed shapes of the carbonyl band in the infrared absorption spectra of 3-phenylsydnone (1-3) and 3-ethylsydnone (4) solutions. Solvent, concentration c (mole/liter), and temperature t (°C): 1—CCl_4, c = 7.2×10^{-4}, t = 12 (curve a) and 50 (curve b); 2—C_6H_6, c = 3.3×10^{-2}, t = 7 (curve a) and 60 (curve b); 3—$CHCl_3$, c = 7.24×10^{-4}, t = 9 (curve a) and 50 (curve b); 4 (curve a)—$CHCl_3$, c = 4.27×10^{-4}, t = 30; curve b—CCl_4, c = 4.76×10^{-4}, t = 30.

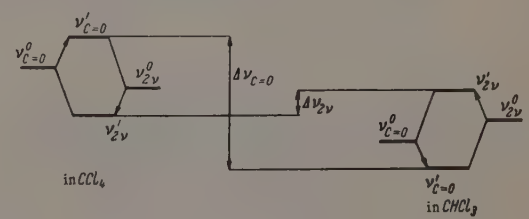
ring, which in both sydnones has the value ~870 cm^{-1}.

It is known[2,3] that the magnitude of the splitting of two accidentally degenerate vibrational levels having the same symmetry is determined, according to second-order perturbation theory for degenerate systems, by the expression

$$\varkappa = \left\{\Delta^2 + 4\left[(H')_e^{v'}\right]^2\right\}^{1/2},$$

where κ is the splitting, Δ is the difference in energy between the unperturbed levels, and $(H')_v^{v'} = \int U_{v'} H' U_v d\tau$ is the matrix element of the perturbation operator. The initially coincident levels with energy E_0 are split into two: $E_{1,2} = E_0 \pm \kappa/2$, with the sign of the correction term determined by the relative position of the unperturbed levels—the higher level is lifted still higher, and the lower one is pushed lower.

By using different solvents, it is possible to shift the carbonyl level toward higher or lower frequencies.[4] In the case of the sydnones, in which the resonating levels are very close, this leads to the carbonyl level disposed sometimes higher (in CCl_4) and sometimes lower (in $CHCl_3$) than the overtone level interacting with it, the location of this latter level depending only weakly on the nature of the solvent. The interacting energy levels in CCl_4 and $CHCl_3$, for example, can be represented by the following schematic diagram:



Here ν^0 are the levels unperturbed by the resonance interaction, and ν' are the perturbed levels.

In this example it can be seen that the carbonyl level is more "mobile" ($\Delta\nu_{C=O} > \Delta\nu_{2\nu}$), since its displacement is caused both by local interaction with the solvent and by the resonance interaction with the overtone. The change in splitting is related to the relative intensities of both components[1,4]: the closer the levels, the more equal the intensities (Fig. 2). Both levels have a mixed character, as a result of which their separation into a carbonyl band and an overtone band is somewhat conditional. This is the case, in particular, of the benzene solution of phenylsydnone, in the spectrum of which both bands have the same intensity at t = +25° (Fig. 2). In other cases we have called the band with the higher intensity the carbonyl band, since this corresponds to a

level in which the state belonging to the unperturbed carbonyl frequency is represented with greater weight.

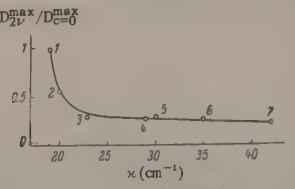


Fig. 2. The ratio $D_{2\nu}^{max}/D_{C=O}^{max}$ as a function of the splitting κ for solutions of 3-phenylsydnone at 25°C. Solvents: 1—benzene, 2—CCl_4, 3—tetrachloroethylene, 4—pyridine, 5—chloroform, 6—ethyl alcohol, 7—phenylsydnone itself, compressed in KBr.

Investigation of the temperature dependence of the band intensity for phenylsidnone in different solvents (temperature interval 5 to 60° and concentration 10^{-3} to 10^{-4} mole/liter) showed that the intensities of the components change markedly with temperature, but the total intensity of both bands varies insignificantly (Fig. 3). A rise in temperature leads to a lessening of the interaction of the ketone with the solvent, which, as is well known, is related to an increase in the carbonyl group vibration frequency. If in addition the levels approach each other (as in $CHCl_3$), the intensities equalize; if they move apart (as in CCl_4), the intensity of the overtone decreases (Fig. 1, curves 3). However, at dilutions of the order of 10^{-2} to 10^{-4} mole/liter only a redistribution of intensity between the resonating levels takes place, and the total integrated intensity is described by a relation of the form $[1 - \exp(-h\nu/kT)]^{-1}$, obtained from statistical considerations.

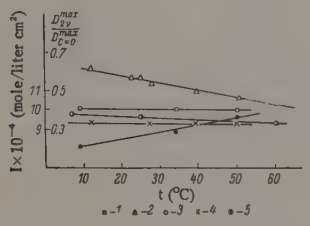


Fig. 3. Temperature dependence of the ratio $D_{2\nu}^{max}/D_{C=O}^{max}$ for the components of the carbonyl band (1, 2) and of their total integrated intensity I (3-5) in phenylsydnone solutions. Solvents: 1, 3—chloroform; 2, 4—CCl_4; 5—benzene.

In the case of Fermi resonance between a carbonyl group and a second order line whose own intensity is insignificant, the true value of the integrated intensity of the carbonyl band is evidently determined by the sum of intensities of both bands (in our work[1] on tropone the true value of intensity was $I_{C=O} = 3.8 \times 10^4$ mole liter^{-1} cm^{-2}).

Frequencies, Splitting Magnitudes, and Maximum Absorption Coefficient Ratios for the Components of the Carbonyl Band of Sydnones in a Number of Solvents (t = 25°C)

Solvent	$\nu_{C=O}$ (cm^{-1})	$\nu_{2\nu}$ (cm^{-1})	$\varkappa$ (cm^{-1})	$\frac{D_{2\nu}^{max}}{D_{C=O}^{max}}$
3-Phenylsydnone				
Benzene	1759 1777		18.0	1
Carbon tetrachloride	1778	1758	20	0.56
Tetrachloroethylene	1781	1758	23	0.28
Pyridine	1753	1782	29	0.26
Chloroform	1750	1780	30	0.29
Ethyl alcohol	1715 1745	1780	35	0.27
Isolated 3-phenylsidnone in crystalline state	1753	1795	42	0.22
3-Ethylsydnone				
Carbon tetrachloride	1771	1745	26	0.24
Chloroform	1747	1769	22	0.53

In conclusion it should be noted that resonance splitting of the carbonyl band is a fairly widespread phenomenon. The presence of the Fermi resonance has been demonstrated, for example, in cyclopentanone,[5] tropone and also, apparently, in sydnones and diphenylcyclopropanone,[6] unsaturated lactones,[7] and in other cases.[4]

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ON THE AUTOMATIC TREATMENT OF ABSORPTION SPECTRA OF ADDITIVE MULTICOMPONENT MIXTURES

V. S. Grinev, O. I. Rau, and G. M. Svishchev (pp. 486-491)

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Certain mathematical questions in the analysis of multicomponent mixtures on the basis of their absorption spectra are considered. On the assumption that all the components are subject to Beer's law and do not interact with each other, and that the experimental errors in the measurement of the optical densities are normally distributed with the same dispersion for all, a set of equations is obtained for the calculation of the concentrations corresponding to the most probable values of the optical densities for the spectra of the separate components and of the mixture being analyzed. Approximate methods are described for solving this set of equations and for estimating the accuracy of the results obtained. Characteristics are presented for a computer program set up to realize the computational scheme described.

RODUCTION

In 1957-1958 the works of Rogoff on the automatic ared analysis of steroid hormone mixtures were pub- ned.[1,2] A specialized analogue computer was con- ucted by the author for the solution of this problem he case of a 6-component mixture. However, Rogoff e only a superficial description of the method.

In the present article, an attempt is made to examine computational scheme which underlies the analysis multicomponent mixtures, with the aim of realizing it a universal digital computer and of estimating the ors in the determination of the concentrations.

TUP AND SOLUTION OF THE PROBLEM

From the transmission spectra of the mixture being lyzed and of the separate components $\Phi(\lambda)$ and $\varphi_i(\lambda)$, pectively, one can determine the optical densities

$$F(\lambda) = -\ln \Phi(\lambda). \tag{1a}$$

$$f_i(\lambda) = -\ln \varphi_i(\lambda). \tag{1b}$$

Let us assume that Beer's law is observed and that components of the mixture do not interact with one ther. Then the optical densities must be additive;

$$F(\lambda) = \sum_{i=1}^{n} x_i f_i(\lambda), \tag{2}$$

ere $x_i = C_i T/c_i t_i$. Here C_i is the concentration of the component in the mixture; T is the cell thickness ring the measurement of the optical density of the mix- e; c_i and t_i are the concentration and cell thickness ring the measurement of the optical density of the i-th mponent in pure form.

If the functions $F(\lambda)$ and $f_i(\lambda)$ were known exactly, determination of the concentrations would reduce to solution of the set of equations (2) for n fixed wave- gths for which the values of F and f_i were linearly ependent.

We shall consider that the experimentally measured ical densities $\tilde{F}(\lambda)$ and $\tilde{f}_i(\lambda)$ are quantities normally tributed with the same dispersion σ around their true ues $F(\lambda)$ and $f_i(\lambda)$.

The problem of the analysis of the spectra of multi- mponent mixtures consists in finding, from the known) and $\tilde{f}_i(\lambda)$, the most probable values of the concentrations C_i. However, in this article we shall limit ourselves to the solution of a simpler problem: the determination of the values of C_i corresponding to the most probable values of the functions $F(\lambda)$ and $f_i(\lambda)$.

These most probable values of the optical densities must satisfy Eqs. (2) and the conditions for a maximum of the probability function.[3]

$$P = \frac{1}{(2\pi\sqrt{2}\sigma)^N} \exp\left\{-\frac{1}{\sigma^2}\sum_{k=1}^{N}\left[(\tilde{F}_k - F_k)^2 + \sum_{i=1}^{n}(\tilde{f}_{ik} - f_{ik})^2\right]\right\},$$

where f_{ik} and F_k are the values of the optical densities $f_i(\lambda)$ and $F(\lambda)$ at the wavelength λ_k, and N is the number of different λ_k's. The choice of the λ_k's is arbitrary, except that, to ensure the independence of the errors $\tilde{F}_k - F_k$ and $\tilde{f}_{ik} - f_{ik}$, the distances between the λ_k's must be greater than the product τv, where τ is the time constant of the recording system and v is the scanning speed.

We denote

$$v = \sum_{k=1}^{N}\left[(\tilde{F}_k - F_k)^2 + \sum_{i=1}^{n}(\tilde{f}_{ik} - f_{ik})^2\right] = \sum_{k=1}^{rN}\left[\left(\tilde{F}_k - \sum_{i=1}^{n} x_i f_{ik}\right)^2 + \sum_{i=1}^{n}(\tilde{f}_{ik} - f_{ik})^2\right]. \tag{3}$$

Then the solution of the problem posed reduces to the solution of the set of equations

$$\frac{\partial v}{\partial f_{ik}} = 0; \quad \frac{\partial v}{\partial x_i} = 0; \qquad \begin{matrix} i = 1, \ldots, n; \\ k = 1, \ldots, N; \end{matrix}$$

i.e.,

$$\sum_{k=1}^{N} f_{ik}\left(\tilde{F}_k - \sum_{j=1}^{n} x_j f_{jk}\right) = 0; \tag{4a}$$

$$\tilde{f}_{ik} - f_{ik} + x_i\left(\tilde{F}_k - \sum_{j=1}^{n} x_j f_{jk}\right) = 0; \tag{4b}$$

$$i = 1; \ldots, n; \; k = 1, \ldots, N.$$

From the set (4b), we obtain

$$f_{ik} = \tilde{f}_{ik} + x_i\left(\tilde{F}_k - \sum_{j=1}^{n} x_j f_{jk}\right). \tag{5}$$

Multiplying both sides by x_i and summing over i, we obtain

$$\sum_{i=1}^{n} x_i f_{ik} = \sum_{i=1}^{n} x_i \tilde{f}_{ik} + \sum_{i=1}^{n} x_i^2 \left(\tilde{F}_k - \sum_{j=1}^{n} x_j f_{jk} \right),$$

whence

$$\sum_{i=1}^{n} x_i f_{ik} = \frac{\sum_{i=1}^{n} x_i \tilde{f}_{ik} + \tilde{F}_k \sum_{i=1}^{n} x_i^2}{1 + \sum_{i=1}^{n} x_i^2}. \qquad (6)$$

Substituting (5) and (6) in (4a), we finally obtain

$$\sum_{k=1}^{N} \left[\tilde{f}_{ik} \left(1 + \sum_{i=1}^{n} x_i^2 \right) \left(\tilde{F}_k - \sum_{j=1}^{n} x_j \tilde{f}_{jk} \right) + x_i \left(\tilde{F}_k - \sum_{j=1}^{n} x_j \tilde{f}_{jk} \right)^2 \right] = 0,$$
$$i = 1, \ldots, n. \qquad (7)$$

The set (7) may be obtained with the help of a simple geometrical interpretation of the expression (3), which generalizes the concept of orthogonal quadratic regression (introduced, for example, in ref. 4) to the case of n variables. Namely, we shall consider v as the sum of the squares of the distances d_k from the points with the coordinates $(\tilde{f}_{1k}, \tilde{F}_k)$ to the points (f_{1k}, F_k) lying on the hyperplane $F - \sum_{i=1}^{n} x_i f_i = 0$. For any x_i, in order to obtain a minimum of v, it is necessary to select those points on the plane which are closest to the points $(\tilde{f}_{1k}, \tilde{F}_k)$; i.e., to measure the distances along the normals to the plane. Then, according to a well-known formula of analytic geometry, we may write

$$v = \sum_{k=1}^{N} d_k^2 = \frac{\sum_{k=1}^{N} \left(\tilde{F}_k - \sum_{i=1}^{n} x_i \tilde{f}_{ik} \right)^2}{1 + \sum_{i=1}^{n} x_i^2}.$$

The requirement of a minimum with respect to x_i will give a set of cubic equations which coincides with the set (7).

However, an exact solution of the set (7) is not feasible in practice. Therefore, it is replaced by approximate solutions. Here we shall examine two possible approximations.

A set of n linear equations. From the set (4), we retain only the equations (4a) with $\tilde{f}_{ik}$ replacing f_{ik} in them. Neglecting in this way the effect of errors in the measurement of f_{ik}, we obtain

$$\sum_{k=1}^{N} \tilde{f}_{jk} \left(\tilde{F}_k - \sum_{i=1}^{n} x_i \tilde{f}_{ik} \right) = 0, \quad j = 1, \ldots, n;$$

or

$$\sum_{i=1}^{n} x_i \left(\sum_{k=1}^{N} \tilde{f}_{jk} \tilde{f}_{ik} \right) = \sum_{k=1}^{N} \tilde{f}_{jk} \tilde{F}_k, \quad j = 1, \ldots, n. \qquad (8a)$$

In ref. 1, it was just the set (8a) which was solved on an analogue computer by one of the iteration methods (just which one was not indicated, nor were its convergence characteristics presented).

Considering the mean-square error in $\tilde{F}_k$ and $\tilde{f}_{ik}$ as known, we find the errors in the coefficients of the set (8a), and then the errors in x_i. For this purpose we write down the set (8a) in the matrix form $\mathbf{Ax} = \mathbf{b}$. Allowing for the errors,

$$(A + \alpha)^{-1} (\mathbf{b} + \beta) = \mathbf{x} + \Delta\mathbf{x}. \qquad (8b)$$

Expanding $(A + \alpha)$ as a series in powers of α and discarding small quantities of higher than first order, we obtain

$$\Delta\mathbf{x} = -A^{-1}\alpha\mathbf{x} + A^{-1}\beta,$$

whence

$$\Delta x_i = -\sum_{j=1}^{n} \sum_{k=1}^{n} a_{ik}^{-1} \alpha_{kj} x_j + \sum_{j=1}^{n} a_{ij}^{-1} \beta_j.$$

Let us introduce the vector $\mathbf{y} = A^{-1} \cdot \mathbf{1}$, which represents a solution of the set (8a) but with the right-hand sides equal to 1. Then

$$y_i = \sum_{j=1}^{n} a_{ij}^{-1}.$$

Assuming $\alpha_{kj} \leq \eta$ and $\beta_j \leq \eta$, and taking account of the fact that the matrices A—and this means A^{-1} also—are symmetric and real positive, we have

$$|\Delta x_i| \leq \eta \sum_{j=1}^{n} \sum_{k=1}^{n} a_{ik}^{-1} x_j + y_i \eta = \eta y_i \left(1 + \sum_{j=1}^{n} x_j \right).$$

Comparing (8a) with (8b) and assuming that the mean-square optical densities

$$\tilde{f}_{\text{av.}\,i} = \sqrt{\sum_{k=1}^{N} \tilde{f}_{ik}^2}$$

are the same for all the spectra, we obtain

$$\alpha_{ik} = \delta A_{ik} = \delta \sum_{j=1}^{N} f_{ij} f_{jk} < \delta \sum_{j=1}^{N} f_{ij}^2 \approx 2\sqrt{N}\, f_{\text{av.}}\, \delta f$$

and

$$\beta_i = \delta b_i = \delta \sum_{j=1}^{N} f_{ij} F_j < \delta \sum_{j=1}^{N} f_{ij}^2 \approx 2\sqrt{N}\, f_{\text{av.}}\, \delta f.$$

Consequently, we may set

$$\eta = -2\sqrt{N}\, \frac{\ln \varphi_{\text{av.}}}{\varphi_{\text{av.}}}\, \delta\varphi, \qquad (1$$

where $\varphi_{\text{av.}}$ is the average transmission for all the spectra and $\delta\varphi$ is the apparatus error.

Finally, we obtain the following estimate:

$$|\Delta x_i| \leq -2\sqrt{N}\, \frac{\ln \varphi_{\text{av.}}}{\varphi_{\text{av.}}} \left(1 + \sum_{j=1}^{n} x_j \right) y_i \delta\varphi. \qquad (1$$

Linearization of the set (7). The set (8a) for x_i coincides with the set of linear normal equations of the least-squares method (for example, ref. 4); i.e., it takes account only of the errors in determining the spectrum of the mixture, $F(\lambda)$. The solution of the set (7), as follows from the method by which it was obtained, takes account also of the errors in determining the spectra of the components, $f_i(\lambda)$; i.e., it is closer to reality.

We have made use of the method of linearized iterations (Newton's method) to solve the set (7).

Let $\Psi(\mathbf{x}) = 0$ be the set (7), $\mathbf{x}$ its exact solution, and $\mathbf{x}_0$ an approximation to it.

$$\mathbf{x} = \mathbf{x}_0 + \xi_0$$

where ξ_0 is the correction.

Then

$$\Psi(\mathbf{x}_0 + \xi_0) = 0.$$

Expanding $\Psi(\mathbf{x}_0 + \xi_0)$ in series form and disregarding terms of higher than first order, we obtain a set of linear equations for ξ_0

$$\Psi(\mathbf{x}_0) + \frac{\partial \Psi(\mathbf{x}_0)}{\partial x} \xi_0 = 0. \qquad (9$$

The approximations will have the form

$$\mathbf{x}_1 = \mathbf{x}_0 + \xi_0; \quad \mathbf{x}_2 = \mathbf{x}_1 + \xi_1 \text{ и т. д.}$$

As soon as the condition

$$\left| \|\mathbf{x}^{k+1}\| - \|\mathbf{x}^{k}\| \right| < \varepsilon,$$

vector $\mathbf{x}^{k+1}$ is taken as the solution.

We choose the solution of the set (8a) as $\mathbf{x}_0$. After stitution of $\mathbf{x}_0$ in (7) and rejection of second-order ntities, a set of n linear equations linking the cor- tion ξ_0 with $\mathbf{x}_0$ is obtained

$$\sum_{k=1}^{N} f_{ik} f_{jk} \xi_i = \sum_{k=1}^{N} \frac{\left(F - \sum_{i=1}^{n} x_{i0} f_{ik} \right)^2}{1 + \sum_{i=1}^{n} x_{i0}^2} x_{j0}; \quad j = 1, \ldots, n. \quad (9b)$$

ARACTERISTICS OF THE COMPUTER PROGRAM

The program for solving the problem was set up for "Ural-1" universal digital computer, operating with xed decimal point. The first part of the program pro- es for the introduction of data, taking of logarithms, ling, and then the solution of the set (8a) by the hod of principal elements[5] and the calculation of y_i.

For the first part of the program,

$$\max n = 24,$$
$$\max (n+1) N = 1300.$$

The second part of the program provides for the so- on of the set (9b)

$$\max n = 14.$$

The relationship of n and N is approximately the me.

The time for solving one variant for $n \leq 8$ takes m 10 to 30 min. A trial run of the programs was car- d out on the steroid infrared spectra presented in . 6.

UNDING-OFF ERRORS

In the present work we do not consider the question he simultaneous distribution of random errors (er- s in the coefficients of the equations) or of rounding- errors, since the number of "spare" digits in the e under consideration is sufficiently large. If the rting ordinates of the spectra are expressed to 3-4 decimal places, rounding-off errors will have no effect up to n = 12-14.

CONCLUSION

The application of a universal digital computer to the analysis of the absorption spectra of complex mixtures enables one to investigate the problem in any direction and in more detail than could be done with an analogue computer.

If a need arises for an analogue computer in one or another field of chemistry for the analysis of a specific class of substances according to their absorption spectra, as being economical and simple in operation, the complete technical requirements for such a computer can be obtained only after consideration of this specific problem with the help of a universal digital computer.

For the practical use of the proposed method for the treatment of spectra, a device is necessary which automatically transforms the ordinates of the spectra into numerical form suitable for introduction into the machine.

The authors thank V. A. Gromov for providing the topic of this investigation, M. R. Shura-Bura and E. S. Lyubimskii for a number of valuable suggestions, and also the crew of the "Ural" machine, on which this work was performed.

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THE LUMINESCENCE OF SIMPLE DERIVATIVES OF BENZENE
I. The Aromatic Amines*

*The paper was presented at the 13th Conference on Spectroscopy at Leningrad in July 1960.

V. L. Ermolaev (pp. 492-497)

Received 14 November 1960

The fluorescence and phosphorescence spectra of aniline, dimethylaniline, diethylaniline, diphenylamine, triphenylamine, indole, carbazole, 9,10-dihydroacridine, and fluorene were measured in solid solution at 77°K. The ratios of the quantum yields of fluorescence and phosphorescence and the phosphorescence decay times of the substances mentioned were determined under identical conditions. The influence of structural factors on the luminescent properties of the compounds studied is discussed. Arguments are examined for and against the interpretation of the long-wavelength absorption and fluorescence bands of the anilines as electron transition spectra.

An investigation of the luminescence of benzene derivatives is of considerable interest from the point of view of finding relationships between the spectroscopic, chemical and photochemical properties of molecules. Such a study is also necessary for an understanding of the processes of absorption and emission of light which take place in more complex molecules. However, there is clearly an insufficient amount of reliable quantitative data available on the luminescent properties of the various benzene derivatives; this situation is probably due to experimental difficulties. Any changes in luminescent properties due to the replacement of a hydrogen in the benzene ring by an amino group are of particular interest, since the amino group is a strong auxochrome, being present in most dyes. In this investigation we observed the spectra and relative yields of the fluorescence and phosphorescence of a number of the simplest amino derivatives of benzene and pyrrole: aniline, N,N-dimethylaniline, N,N,-diethylaniline, diphenylamine, triphenylamine, 9,10-dihydroacridine, indole, carbazole, and the hydrocarbon analog of the latter (fluorene) in solid solution at 77°K.

EXPERIMENTAL METHOD

The spectra and luminescence yields were measured with a wide-aperture photoelectric recording instrument which had been calibrated for spectral sensitivity on the frequency scale with the aid of a tungsten ribbon lamp.[1,2] The excitation was accomplished by means of mercury lines isolated with the aid of a grating monochromator. The phosphorescence spectra were measured both under continuous excitation and with the aid of a two-disc Becquerel phosphoroscope. The spectral width of the monochromator slits was less than 100 cm^{-1} during all the measurements of luminescence spectra; this is appreciably narrower than the bands investigated. All the spectra presented have been converted to quantum spectral distributions of intensity on a frequency scale. Measurements of the phosphorescence decay times ($\tau_{phos.}$) were carried out on equipment consisting of a single special shutter described in the article by Pilipovich and Sveshnikov,[3] a 6H8* double triode amplifier and an H-700 magnetic oscillograph. The fact that the oscillograph records on wide paper (120 mm) and prints time marke makes it very convenient for measuring $\tau_{phos.}$ values from 0.1 to several tens of seconds with an accuracy of 3-5%. The purity of the materials studied was checked in terms of melting and boiling points and also spectroscopically. The aniline, N,N-dimethylaniline, and N,N-diethylaniline were distilled in air over zinc powder. The diphenylamine, triphenylamine, and 9,10-dihydroacridine were sublimed in a high vacuum. The indole was recrystallized twice from a mixture of water and alcohol. The carbazole and the fluorene were the pures (Kahlbaum Company).* In order to eliminate the effects of reabsorption and association the measurements were conducted at concentrations of 10^{-4}-10^{-5} M. The following substances, used as solvents, freeze in a glassy for at 77°K: a 2:1 mixture of ethyl alcohol and diethyl ethe by volume (referred to below as a. + e.), petroleum ethe (p.e.), and dibutyl ether. The purification of a. + e. and p.e. has been described previously.[1,2,4] The dibutyl ethe was washed repeatedly with a water solution of NaCl, dried with sodium, and distilled.

*The author is very grateful to T. K. Razumova and G. O. Karapetyan for giving him the amplifier.

*The author wishes to thank V. V. Perekalin, B. Ya. Sveshnikov, A. S. Cherkasov, and I. M. Stroiman for su plying the materials.

EXPERIMENTAL RESULTS

The fluorescence and phosphorescence spectra of the aromatic amines and pyrrole derivatives which we studied are shown in Figs. 1 and 2. They are appreciably displaced toward the lower frequencies and quite diffuse compared to the corresponding spectra of methy and halogen derivatives of benzene.[5,6] While the fluores cence spectra of benzene and its methyl derivatives in solid solution consist of rather narrow bands, the fluorescence spectra of aniline, dimethylaniline, diethylani line, diphenylamine, and triphenylamine in a. + e. are a most completely featureless (Fig. 1). A fairly distinct structure is observed only in the fluorescence spectrun of diethylaniline in p.e. The fluorescence spectra of ind and carbazole have structure, however, it is rather diff compared to the hydrocarbon analog of carbazole—fluorene (Fig. 2). The phosphorescence spectra of the aro-

atic amines studied have more structure than the fluo-scence spectra (Figs. 1 and 2) which indicates con-derable broadening of the fluorescence levels. We re not able to make a reliable measurement of the minescence spectra of compounds containing N—H oups in p.e. because of the low intensity of the radia-on in this case. This indicates the presence of quench-g processes brought about either by internal causes by association. We note that the presence of pyridine aliphatic amines in the solution quenches the lumi-scence of the compounds mentioned.

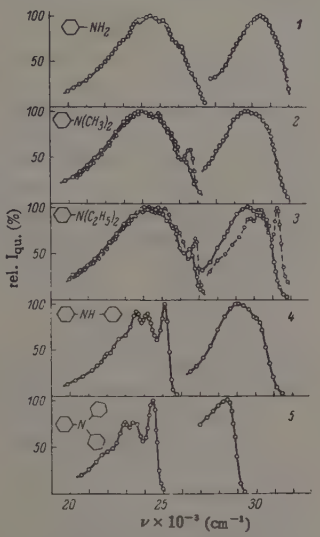


Fig. 1. Fluorescence (on the right) and phosphorescence (on the left) spectra of solutions of aromatic amines at 77°K. Material: 1—aniline; 2—N,N-dimethylaniline; 3—N,N-diethylaniline; 4—diphenylamine; 5—triphenylamine. Solvent: light points (solid lines)—a. + e.; dark points (dashed lines)—p.e. Excitation by Hg 3030 and 3130 A.

Data on the relative quantum yields of phosphores-nce and fluorescence ($\eta_{phos.}/\eta_{fl.}$) and decay times of e phosphorescence ($\tau_{phos.}$) of the same compounds are own in the table. It is seen from the table that the $_{hos.}/\eta_{fl.}$ values of the aromatic amines are increased en the hydrogen bound to the nitrogen atom is re-aced by an aliphatic radical (methyl or ethyl). An even eater increase in the value of $\eta_{phos.}/\eta_{fl.}$ is observed the order aniline, diphenylamine, and triphenylamine. the same time, the phosphorescence decay time of the omatic amines is shortened when the hydrogen bound the nitrogen is replaced by an alkyl or phenyl radical ee the fourth column of the table). The $\eta_{phos.}/\eta_{fl.}$ and $_{hos.}$ values of the aromatic amines are not changed by ore than 20% when dibutyl ether and p.e. are used as lvents in place of a. + e. (measurements in p.e. were ade only for dimethyl- and diethylaniline).

We attempted to estimate the absolute quantum yield the radiation of several of the aromatic amines studied comparing the intensities of their fluorescence with e fluorescence intensity of naphthalene at 77°K with dentical absorption. Gilmore, Gibson, and McClure[7] had reviously measured the absolute fluorescence quantum ield of a solution of naphthalene in an ether-isopentane-lcohol mixture as equal to 0.55 at 77°K. Our measure-

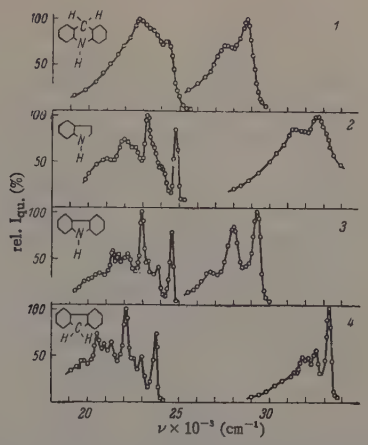
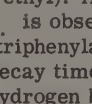
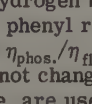
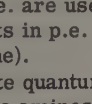
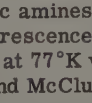
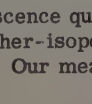


Fig. 2. Fluorescence (right) and phosphorescence (left) spectra of solutions of aromatic amines in a. + e. at 77°K. Materials: 1—9,10-dihydroacridine; 2—indole; 3—carbazole; 4—fluorene. Solvent: see the note under Fig. 1. Excitation: 1, 3—λ = 3030 and 3130 A; 2, 4—λ = 2800-2600 A.

ments indicated that this value is apparently too high, however, since the total luminescence quantum yields of the amines which were obtained using these data for the fluorescence yield of naphthalene turned out to be 20-40% greater than unity. Hence, all we can say about the absolute quantum yields of the total luminescence of the aromatic amines investigated is that they are high and apparently close to one. Data on the frequencies (probabilities) of radiating transitions in several amines are shown in the fifth column of the table. These were estimated according to the area of the first absorption bands of the compounds mentioned and were taken from the literature.[8,9]

Material	Structural formula	$\frac{\eta_{phos.}*}{\eta_{fl.}}$	$\tau_{phos.}$ (sec)	$1/\tau_a$ (sec^{-1})	$\frac{r_{^1\Gamma^*\to{}^1\Gamma}}{(sec^{-1})}$
Aniline		3.1±0.2	4.2±0.2	$4.1 \cdot 10^7$	$1.3 \cdot 10^8$
N, N-Dimethyl aniline		4.2±0.2	2.4±0.1	$6.5 \cdot 10^7$	$3 \cdot 10^8$
N, N-Diethyl aniline		6.1±0.3	2.0±0.2	$6.5 \cdot 10^7$	$4 \cdot 10^8$
Diphenylamine		7.3±0.4	1.9±0.1	$7 \cdot 10^8$	$5 \cdot 10^9$
Triphenylamine		15±1	0.70±0.05	—	—
9, 10-Dihydro-acridine		1.6±0.2	3.5±0.2	—	—
Indole		0.36±0.03	6.3±0.2	—	—
Carbazole		0.55±0.05	7.6±0.3	—	—
Fluorene		< 0.05	6.9±0.3	—	—

*All data are for a. + e. at 77°K.

DISCUSSION OF RESULTS

The frequency of internal conversion from the fluorescent state ($^1\Gamma^*$) to the phosphorescent state ($^3\Gamma$) can be estimated from the ratio of the phosphorescence yield to the fluorescence yield (if the frequency of the radiating transition corresponding to fluorescence and the absolute luminescence quantum yield are also known). We propose the term "intercombination" conversion ($^r{}^1\Gamma^* \rightarrow \Gamma^3$) for designating this transition. Estimates of this quantity, made under the assumption that there is no quenching in the phosphorescence level, are shown in the last column of the table. As is seen from the table, the frequency of intercombination conversion in the amino derivatives of benzene is two orders of magnitude greater than in the hydrocarbons—benzene ($r \sim 10^6$ sec^{-1}), naphthalene ($r \sim 2 \times 10^5$ sec^{-1}), and its methyl derivative ($r \sim 5 \times 10^5$ sec^{-1}). Although there are no data in the literature for toluene, in all probability its r value is close to that of benzene. On the other hand, however, the $\tau_{phos.}$ values of aniline, dimethylaniline, and diethylaniline are nearly the same as that of benzene and its methyl derivatives (4-8 sec).[10] It can be concluded from this that the spin-orbital coupling in the aromatic amine molecules in the triplet state is nearly the same as that in benzene, whereas in the fluorescent state, the spin-orbital coupling in the amines is two or three orders of magnitude stronger than in benzene and its methyl derivatives. It is evident that the nonbonding electrons of the nitrogen atom play an active role in the enhancement of spin-orbital coupling in the fluorescent state of the aromatic amines. It is interesting to note that the introduction of a nitrogen atom on the naphthalene ring (quinoline) also leads to an increase of two orders of magnitude in the frequency r, and to a very slight increase in the probability of a radiating transition from the triplet level.[1,2,11] It was shown in these same references that a decrease in the spin-orbital coupling in the fluorescent state occurs when the nitrogen atom of the quinoline enters into a hydrogen bond.

The reason for the increase in spin-orbital coupling on replacement of a hydrogen atom in an amino group by an alkyl or phenyl radical is not clear as yet, although an increase in the relative phosphorescence yield was observed by Zelinskii et al.[12] when the imide hydrogen in phthalimides was replaced by methyl or phenyl. It cannot be concluded from this, however, that the replacement of hydrogen by alkyl or phenyl always increases spin-orbital coupling in molecules. It was established in ref. 4 that the replacement of hydrogen in the aldehyde group of benzaldehyde by an alkyl (phenyl methyl ketone, ethyl phenyl ketone) or a phenyl (diphenyl ketone) radical increases its phosphorescence decay time, that is, it reduces the spin-orbital coupling in the molecules. In the case of the introduction of the phenyl group it can be objected that the system of conjugate bonds in the diphenylamine is sharply different from those of aniline; however, both the great similarity of the fluorescence and phosphorescence spectra and data on the polarization of the fluorescence[13] give evidence to the contrary.

The nature of the lower excited levels of aniline and its derivatives remains unclear at the present time. A number of authors[14] are of the opinion that the long-wavelength absorption band of the anilines near 2800 A is a displacement of the long-wavelength absorption band of benzene (2500 A) caused by the substituent. On the other hand, Klevens and Platt[15] developed an analogy between the first benzene absorption band and the second aniline band (at 2400 A). Finally, a number of authors[16] in the past have interpreted several bands in molecular absorption spectra (the anilines among them) as electron transfer bands. There are several of the special features of the luminescence of the aromatic amines (the continuous character of the fluorescence spectrum and the high phosphorescence yield) which are not in disagreement with such an interpretation. The fact that the long-wavelength absorption band of the aromatic amines disappears in acid media[14] is also in agreement with them. On the other hand, an examination of the structure of the fluorescence spectra of the aromatic amines in solid solutions shown in Figs. 1 and 2 (in those cases when it appears) and also the vibrational structure of the fluorescence spectra of aniline in vapors obtained by Vartanyan[17] indicates that vibrational frequencies appear in the fluorescence and phosphorescence of aromatic amines which are close to the frequencies in the luminescence spectra of the methyl derivatives of benzene (1000 and 1580 cm^{-1}). Although the development of vibrational frequencies characteristic of the benzene ring can also be expected in the case of an electron transfer spectrum since the appearance in the benzene ring of an additional electron in a bonding or nonbonding orbit must lead to a change in the equilibrium configuration of the atoms of the ring in the excited state this would, however, require that there appear in the spectrum, in addition to these frequencies, a frequency corresponding to a valence vibration C—N (1200-1350 cm^{-1})[18] which has a greater intensity. The only case in which this vibration will not appear is when the equilibrium spacing of the C—N in the excited state has the same value as in the ground state. The latter has a low probability for an electron transition corresponding to the transfer of an electron. The question of the extent of the redistribution of electron density in the excited state can be solved by measuring the change in the value of the dipole moment of the molecule on undergoing a transition to the excited state. An investigation of the effect of the solvent on the absorption and fluorescence spectra (at 293°K) and treatment of the data by the method of Neporent and Bakhshiev[19] can yield information on the magnitude of such changes.

In order to predict the possible kinds of photochemical reactions, it is essential to obtain data concerning the types of excited states of the molecules and, consequently, about the redistribution of electron density in the fluorescent and phosphorescent states in comparison to the ground state. For example, in the case of electron transfer from the substituent to the ring with excitation, photochemical reactions with electrophilic agents should be expected, leading to a substitution in the ring. In the case of electron transfer in the opposite direction with absorption of light, reactions of substitution by nucleophilic agents on the ring must take place. It is clear from what has been said that it is essential to determine the character of the long-wavelength transition in aromatic molecules in order to understand the fundamental photochemical processes.

In conclusion, I consider it my pleasant duty to thank my teacher, Academician A. N. Terenin, for his help in this investigation.

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THE INFLUENCE OF THE REABSORPTION OF LIGHT ON THE SPECTRAL DEPENDENCE OF PHOTOCONDUCTIVITY IN MOLECULAR CRYSTALS

V. M. Agranovich and Yu. V. Konobeev (pp. 498-503)

Received 31 October 1960

It is demonstrated that the occurrence of reabsorption in an anthracene crystal increases the magnitude of the photocurrent and noticeably modifies its spectral curve.

TRODUCTION

Although the photoconductivity of organic compounds been known for a long time,[1] most of the experimental sults pertaining to this interesting effect were obtained hin the last 10 years.[2-5] In all crystals of aromatic drocarbons investigated so far the photocurrent has rresponded to the edge of allowed exciton absorption nds characterized by high intensity. Since the levels ich correspond to these bands are lower than the levels ionized states with a free electron, it is assumed that otoconductivity arises from the formation of current rriers by "neutral" excitons. In this case, the num- r of the latter must depend essentially on the concen- ation of excitons, regardless of the mechanism by ieh the carriers are formed.

Considerable overlapping of absorption and emission ectra occurs in many crystals (and particularly in an- acene), leading to more reabsorption. Reabsorption creases the photon lifetime in the crystal, and con- quently increases the total number of excitons. Re- sorption also has an influence on exciton distribution depth. As a result, there is a decrease or an increase the number of excitons at high or low concentration es, respectively. An increase in the total number of citons present in the sample, if caused by reabsorp- n, must be accompanied by an increase in photocur- nt. The "spreading" of the exciton distribution func- on in depth can, on the other hand, influence the extent competition between recombination processes among charge carriers which are linearly or quadratically dependent on concentration.

In order to examine the reabsorption effect, we will use the model of volume conductivity in anthracene proposed in ref. 4. It was shown in this reference that it is sufficient to make the following assumptions in order to explain most of the effects observed in anthracene: (a) positive charge carriers are more mobile than negative carriers; (b) only carrier neutralization takes place at the electrodes; this process is not accompanied by any replenishment of the number of carriers; (c) charge carriers are formed only at spots where light energy is absorbed.

If we also assume that carrier diffusion is slower than recombination and trapping, we can write an equation for the concentration of electrons n and holes p in the form:

$$\left.\begin{aligned} \frac{dn}{dt} &= Ac(x,\ t) - \frac{n}{\tau_n} - \alpha np. \\ \frac{dp}{dt} &= Ac(x,\ t) - \frac{n}{\tau_p} - \alpha np. \end{aligned}\right\} \qquad (1)$$

In these equations c(x, t) is the exciton concentration at a depth x at time t, τ_n and τ_p are the electron and hole lifetimes for trapping, α is an electron-hole recombination coefficient. With constant illumination, c(x, t) = c(x) and dn/dt = dp/dt = 0. The meaning of coefficient A depends essentially on the mechanism leading to the formation of charged current carriers instead of an exciton.

Lyons, for example, assumed that excitons first form an ion pair, localized at neighboring lattice points, and that this ion pair later produces a free electron and a hole as a result of thermal dissociation. The coefficient A then turns out to be equal to

$$A = w_1 w_2 \tau, \qquad (2)$$

where w_1 is the probability of exciton disintegration as a result of which a bound ion pair is formed, w_2 is the probability for the dissociation of a bound ion pair to give free electrons and a hole, and τ is the lifetime of the polaron state (electron and hole at neighboring lattice points). The disintegration of the polaron state with the formation of free charge carriers can take place in several steps. Several activation energies are involved in this case, and Eq. (2) takes another form. This complication does not change the form of Eq. (1), however, and we will not consider it further.

The abovementioned investigations[2-5] indicate that the magnitude of the photocurrent strongly depends on the direction of the applied electric field. The photocurrent is found to be greater when the illuminated electrode is positive. This is due to the comparatively greater mobility of positively charged carriers. As a result, no large space charge is formed, as is the case when the illuminated electrode is negative. It can therefore be assumed that when the illuminated electrode is positive, the electron and hole concentrations in the illuminated volume are approximately equal (n = p). In this approximation, the photocurrent is directly proportional to the total number of negative minority carriers present in the crystal. The concentration of these carriers is determined by:

$$Ac(x) = \frac{n(x)}{\tau_n} + an^2(x). \qquad (3)$$

Let us examine two limiting cases. Let the concentration of carriers be limited in the first case by trapping, and in the second case by the electron-hole recombination process. The current I can be expressed for both limiting cases as follows:

$$I_q^{I} = \beta A \tau_n \int_0^{\infty} c(x)\, dx, \qquad (4)$$

$$I_q^{II} = \beta \sqrt{\frac{A}{\alpha}} \int_0^{\infty} \sqrt{c(x)}\, dx. \qquad (5)$$

In these limiting cases, the spectral dependence of the current is thus determined by the exciton distribution in depth.

EXCITON DISTRIBUTION IN DEPTH

The exciton concentration in molecular crystals satisfies an integral-differential equation which has been examined in a number of references[6,7] in connection with a study of the problem of the influence of the migration of electron excitation energy on the luminescence of molecular crystals. Reference 6 showed that in anthracene, reabsorption is the principal process which determines the distribution of excitons in crystals which are not too thin ($d \gg 2\mu$). Under these conditions, the diffusion term in the kinetic equation, satisfied by the function c(x), can be neglected. For the sake of simplicity, we will also ignore the effects related to the reflection of luminescent light from the surfaces of the crystal. Under these assumptions, in the case of a steady state, the equation for the function c(x) will assume the form

$$Pc(x) = \Phi_0 \bar{k} e^{-\bar{k}x} + \frac{P}{4\pi} \int_0^{\infty} d\nu E(\nu)\eta(\nu)k(\nu) \int_V c(x_1) \frac{e^{-k(\nu)|r-r_1|}}{|r-r_1|^2}\, dr_1.$$

Where P is the total probability of the disappearance of the exciton per second; $\eta(\nu)$ is the quantum yie of anthracene luminescence when excited with light of t frequency ν (not the technical, but the "true" yield); $E(\nu) = \rho(\nu)/\int_0^{\infty} \rho(\nu)d\nu$ where $\rho(\nu)$ is the probability per u time of a process resulting in the decomposition of the exciton with emission of a photon of frequency ν, integrated over all angles; $\bar{k}$ is the absorption coefficient light falling on the crystal normal to the surface, from the side of negative values of x. Let us introduce the d mensionless quantities $z = k_0 x$, $z_0 = k_0 d$, $\gamma = \bar{k}/k_0$, $c(z) = Pc(x)/\Phi_0 \bar{k}$, $b(\nu) = k(\nu)/k_0$, and $a(\nu) = \frac{1}{2}E(\nu)\eta(\nu)$ where k_0 is the absorption coefficient of the light which is reabsorbed most strongly in anthracene. Equation (6) can b rewritten in new notation as follows:

$$c(z, \gamma) = e^{-\gamma z} + \int_0^{\infty} a(\nu) b(\nu)\, d\nu \int_0^{z_0} c(z_1, \gamma) E_1(b(\nu)|z - z_1|)\, dz_1,$$

where

$$E_1(z) = \int_1^{\infty} \frac{e^{-z\xi}}{\xi}\, d\xi.$$

We will henceforth use an approximate method for the solution of Eq. (7), proposed in ref. 7, according to which the function $E_1(z)$ is replaced by a simpler kern of the type $\mu e^{-\mu z}$, where $\mu = 3$ is determined by minimizing $\int_0^{\infty} [E_1(z) - \mu e^{-\mu z}]^2 dz$. We will, moreover, limit ourselves to a q-approximation (see ref. 7). Equation (7) is considerably simplified as a result of the assumptions made, and takes the form

$$c(y, \eta) = e^{-\eta y} + \frac{q}{2} \int_0^{z_0} c(y_1, \eta) e^{-|y - y_1|}\, dy_1.$$

Here

$$\eta = \frac{\gamma}{\mu}, \quad z = \frac{y}{\mu}, \quad z_0 = \frac{y_0}{\mu}.$$

For anthracene,[6] q = 0.72. It is easy to see that the integral equation (7) is equivalent to a differential equatio of second order

$$\frac{d^2c}{dy^2} - (1 - q)c = (\eta^2 - 1)e^{-\eta y}$$

with the boundary conditions

$$\left.\begin{aligned} c(0, \eta) &= c'(0, \eta) + \eta + 1, \\ c(y_0, \eta) &= -c'(y_0, \eta) + (1 - \eta)e^{-\eta y_0}. \end{aligned}\right\}$$

The desired solution of integral equation (7) can th be represented as follows ($\delta^2 = 1 - q$):

$$c(y, \eta) = Ne^{-\delta y} + Me^{\delta y} + \frac{\eta^2 - 1}{\eta^2 - \delta^2} e^{-\eta y},$$

The coefficients N and M which enter into this expres sion are determined from boundary conditions (9). As result, we obtain the following terms:

$$= \frac{1}{\Delta}\frac{1-\delta^2}{\tau_1^2-\delta^2}[(1+\tau_1)(1-\delta)e^{-\delta y_0} - (1+\delta)(1-\tau_1)e^{-\eta y_0}], \quad (11)$$

$$= \frac{1}{\Delta}\frac{1-\delta^2}{\tau_1^2-\delta^2}[(1-\delta)(1-\tau_1)e^{-\eta y_0} - (1+\delta)(1+\tau_1)e^{\delta y_0}], \quad (12)$$

ere

$$\Delta = (1-\delta)^2 e^{-\delta y_0} - (1+\delta)^2 e^{\delta y_0}.$$

Expressions (11) and (12) are simplified when the kness of the crystal d is sufficiently great that the qualities $\delta y_0 \gg 1$, $\eta y_0 \gg 1$ are fulfilled. In this iting case,

$$\left.\begin{aligned} M &= 0, \\ N &= \frac{(1+\tau_1)(1-\delta)}{\tau_1^2-\delta^2}. \end{aligned}\right\} \quad (13)$$

Substitution of Eq. (10) into Eqs. (4) and (5) enables to obtain the desired spectral dependence of the photo-rent in both limiting cases, when the carrier concen-ion is limited by trapping [Eq. (4)] or by the hole-ctron recombination process [Eq. (5)].

In the case of no reabsorption (q = 0) the function $\Phi(\bar{k}) = \Phi_0 \bar{k} e^{-\bar{k}x}/P$. Substituting this function into Eqs. and (5) we obtain

$$I^{I}_{q=0} = \beta A \tau_n \frac{\Phi_0}{P}(1 - e^{-\bar{k}d}) \quad (14)$$

$$I^{II}_{q=0} = \beta \sqrt{\frac{A\Phi_0}{aP\bar{k}}}\left(1 - e^{-\frac{\bar{k}}{2}d}\right) \quad (15)$$

pectively. The ratio $I_q/I_{q=0}$ was calculated for a ntitative evaluation of the reabsorption effect in an-acene, under the assumption that the conditions of ap-ability of Eqs. (13) are fulfilled. Results of the cal-ation are shown in Fig. 1. It follows from the data ained that reabsorption in anthracene increases the tocurrent two-fourfold, depending on the value of the

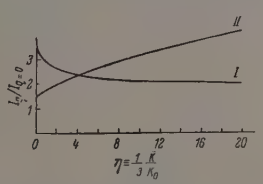

Fig. 1. Values of the ratios $I^{I}_{q}/I^{I}_{q=0}$ (curve I) and $I^{II}_{q}/I^{II}_{q=0}$ (curve II).

sorption coefficient of incident light, and also on which the carrier recombination processes is the principal e. In order to compare the theoretical results with periment, we used data obtained in ref. 4 and repre-nted in Fig. 2. It follows from this figure that photo-rrent minima correspond to maxima of the absorp-n coefficient at wavelengths smaller than 4000 A. reover, as shown in ref. 4, the photocurrent in this velength range is proportional to the square root of intensity of light incident on the crystal. These ob-rvations led the authors of ref. 4 to the conclusion that ctron-hole recombination is the process which limits carrier concentration in the indicated wavelength nge (we are always talking here about phenomena oc-rring when the positive electrode is illuminated). In s case, if there were no reabsorption, the photocur-nt should be inversely proportional to the square root the absorption coefficient of the light incident on the

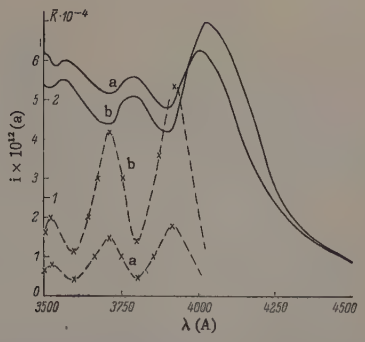

Fig. 2. Spectral dependence of volume photocurrent i (solid curves) and absorption spectra $\bar{k}$ (dashed curves) of an anthracene single crystal for two directions of light polarization (a,b). The positive electrode is illuminated.

crystal [see Eq. (15)]. It must be kept in mind that crystals 1-4 mm thick were used to obtain the experimental data shown in Fig. 2, and that the exponential term in Eq. (15) can therefore be neglected in the spectral region under consideration. Values of the product $I\sqrt{\bar{k}}$,* obtained

*In arbitrary units.

from the data of Fig. 2* for wavelengths shorter than

*The points used to calculate the product $I\sqrt{\bar{k}}$ (Fig. 3) are marked by crosses in Fig. 2.

4000 A, are shown in Fig. 3. If reabsorption were negligible, the corresponding points would fall on a horizontal straight line. Actually (as in curve II, Fig. 1) the points lie on a curve which rises as the absorption coefficient increases. To within experimental accuracy, the ratio of experimental values of $I\sqrt{\bar{k}}$ corresponding to large and small values of the light absorption coefficient is in satisfactory agreement with the theory. In both cases,

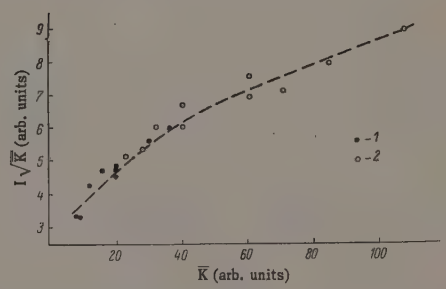

Fig. 3. Dependence of $I\sqrt{\bar{k}}$ on $\bar{k}$. Polarization of light: 1—a; 2—b (see Fig. 2).

this ratio is approximately equal to 2.5. In order to obtain a more quantitative comparison of theoretical and experimental results, it is necessary to know the absorption coefficient of the light reabsorbed most strongly in the samples investigated in ref. 4.*

*Generally speaking, carrier diffusion should also be taken into account. This effect appears to be small in the wavelength range examined, because the photocurrent in this region is proportional to the square root of the incident light intensity.

Let us mention in conclusion that the considerable influence of reabsorption on the photoconductivity of anthracene confirms the hypothesis of an exciton mechanism of photoconductivity in molecular crystals. One must keep in mind, however, that the process of carrier generation resulting from exciton disintegration should be investigated separately.

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REABSORPTION IN CRYSTALS OF FINITE THICKNESS. III

Yu. V. Konobeev (pp. 504-512)

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A theory of light reabsorption in molecular crystals is presented. Formulas are obtained for the average true luminescence decay and rise times in the nonstationary case (decay and rise of luminescence). Various asymptotic cases are investigated in detail. The results obtained in the present paper for nonstationary processes can be applied to the theory of radiation energy transfer in planetary atmospheres and to the theory of neutron moderation.

In ref. 1, a phenomenological theory was developed to describe the migration of the electron excitation energy in molecular crystals of finite thickness. On the basis of equations given in this paper, formulas were obtained in ref. 2 for the quantum yield and the average "exponential" decay time of luminescence, the latter being determined by the formulas

$$\tau_{0,d}^{(\nu)}(\gamma)=\frac{\int_0^\infty I_{0,d}^{(\nu)}(\tau)\,d\tau}{I_{0,d}^{(\nu)}(0)}. \qquad (1)$$

$I_0^{(\nu)}(\theta,\tau)$ and $I_d^{(\nu)}(\theta,\tau)$ are the numbers of photons in the frequency range $d\nu$ which leave the crystal per second per cm^2 of surfaces, $x = 0$ and $x = d$, per unit of solid angle at an angle θ to the external normal. The quantities $I_0^{(\nu)}(\theta,\tau)$ and $I_d^{(\nu)}(\theta,\tau)$ are determined by the following formulas:

$$I_0^{(\nu)}(\theta,\tau)=\frac{\rho(\nu)\,[1-r_\nu(\cos\theta)]\,\Phi_0}{4\pi P k_0}\,R\,[b(\nu)\sec\theta,\ \gamma], \qquad (2)$$

$$I_d^{(\nu)}(\theta,\tau)=\frac{\rho(\nu)\,[1-r_\nu(\cos\theta)]\,\Phi_0}{4\pi P k_0}\,e^{-b(\nu)z_0\sec\theta}R\,[-b(\nu)\sec\theta,\ \gamma]. \qquad (3)$$

In these formulas

$$R(\xi,\gamma)=\int_0^{z_0} e^{-\xi z}c(z,\gamma)\,dz; \qquad (4)$$

$\rho(\nu)$ is the density of the over-all probability for the emission of a quantum $\hbar\nu$ per second in any direction as a result of exciton decay; $\tau = Pt$, where P is the over-all probability per second for the disappearance of an exciton; Φ_0 is the total number of excitons created by the exciting light flux per cm^2 of the area $x = 0$; $r_\nu(\cos\theta) = \sum_{n=0}^{\infty} a_n^{(\nu)}\cos^n\theta$ is the reflection coefficient for luminescence of frequency ν falling on the crystal surface from the inside at the angle θ; $b(\nu) = k(\nu)/k_0$, $k(\nu)$ is the absorption coefficient for light of frequency ν; $\gamma = k/k_0$, $k = \bar{k}/\cos\theta_0$, where $\bar{k}$ is the absorption coefficient of light falling on the crystal at the angle θ_0; $c(z,\tau) = Pc_1(\mathbf{r},t)/\Phi_0$, where $c_1(\mathbf{r},t)$ is the exciton concentration at point $\mathbf{r}$ at the instant t; $z_0 = k_0 d$, where d is the thickness of the crystal and k_0 is the absorption coefficient of light for the most strongly reabsorbed frequency (for details see ref. 1).

The present investigation is a continuation of the work described in ref. 2. New exact expressions will be derived for the true decay time of luminescence, defined by the following formula:

$$T_{0,d}^{(\nu)}(\gamma)=\frac{\int_0^\infty I_{0,d}^{(\nu)}(\tau)\,\tau d\tau}{\int_0^\infty I_{0,d}^{(\nu)}(\tau)\,d\tau}.$$

When the decay law of luminescence is strictly exponential with respect to time, $\bar{\tau}_0^{(\nu)} = T_0^{(\nu)}$ and $\bar{\tau}_d^{(\nu)} = T_d^{(\nu)}$. The degree of deviation of the true decay law from the exponential law can be inferred from the difference between $\bar{\tau}_{0,d}^{(\nu)}$ and $T_{0,d}^{(\nu)}$.

As in refs. 1 and 2, we will discuss here only phosphors in which the reflection of luminescence from inner surfaces can be neglected. We will furthermore assume that the diffusion length $\sqrt{D/P}$, where D is the diffusion coefficient for excitons, is much smaller than the migration length of the energy of electron excitation, caused by reabsorption.

Let us note that in the case of such phosphors there is no sense in separately investigating the rise and the decay times of luminescence, since these agree in magnitude. This conclusion results from the following considerations: It was shown in ref. 1 that the function $c(z,\tau)$ satisfies (in the q-approximation, see ref. 1) the equation:

$$\frac{\partial c}{\partial\tau}=-c+e^{-\gamma z}+\frac{q}{2}\int_0^{z_0} c(z_1,\tau)\,E_1(|z-z_1|)\,dz_1.$$

Let us call $c_0(z, \gamma)$ the solution of Eq. (6) for the ionary case ($\partial c/\partial \tau = 0$).

$$E_1(z) = \int_1^\infty \frac{e^{-z\xi}}{\xi}\, d\xi.$$

Knowing the solution of Eq. (6) and the function $\gamma)$, we must calculate the average "exponential" e time according to the formula

$$\tau'^{(\nu)}_{0,d} = \frac{\int_0^\infty (I^{(\nu)\,\text{stat.}}_{0,d} - I^{(\nu)}_{0,d}(\tau))\, d\tau}{I^{(\nu)\,\text{stat.}}_{0,d}}, \qquad (7)$$

the average true rise time according to the formula:

$$T'^{(\nu)}_{0,d} = \frac{\int_0^\infty (I^{(\nu)\,\text{stat.}}_{0,d} - I^{(\nu)}_{0,d}(\tau))\, \tau d\tau}{\int_0^\infty (I^{(\nu)\,\text{stat.}}_{0,d} - I^{(\nu)}_{0,d}(\tau))\, d\tau}. \qquad (8)$$

If Eq. (6) is subtracted term by term from the equa- defining the function $c_0(z, \gamma)$, the equation obtained, cifying the difference $c_0(z, \gamma) - c(z, \gamma, \tau)$, corresponds tly to the equation which determines the exciton con- tration during decay. It therefore follows that the func- $c_0(z, \gamma) - c(z, \gamma, \tau)$ is a solution of Eq. (6) in which term $e^{-\gamma z}$ has been omitted. Consequently, Eqs. (1), (7), and (8) give $\overline{\tau}^{(\nu)}_{0,d} = \overline{\tau}'^{(\nu)}_{0,d}$ and $\overline{T}^{(\nu)}_{0,d} = \overline{T}'^{(\nu)}_{0,d}$. From e on, we will be speaking only of the fluorescence ime of the crystal.

(a) In order to calculate the average true fluores- ce lifetime of the crystal, it is necessary, as seen n Eqs. (2)-(5), to know the function

$$\Psi(\eta, \gamma, z_0) = \int_0^{z_0} e^{-\eta z} \psi(z, \gamma, z_0)\, dz, \qquad (9)$$

where the function $\psi(z, \gamma, z_0)$ is defined by the expression $\psi(z, \gamma, z_0) = \int_0^\infty \tau c(z, \gamma, z_0, \tau) d\tau$ and $c(z, \gamma, z_0, \tau)$ is the solution of Eq. (6) without the $e^{-\gamma z}$ term on the right. It can be shown by a method reported in detail in ref. 1 that the function $\psi(z, \gamma, z_0)$ satisfies

$$\psi(z, \gamma, z_0) = \varphi(z, \gamma, z_0) + \frac{q}{2} \int_0^{z_0} \psi(z_1, \gamma, z_0) E_1(|z - z_1|)\, dz_1, \qquad (10)$$

where the function $\varphi(z, \gamma, z_0)$ is a solution of Eq. (10), but on the right side of which the nonhomogeneity appears as the function $c_0(z, \gamma, z_0)$ instead of the function $\varphi(z, \gamma, z_0)$. The function $\Psi(\eta, \gamma, z_0)$ is defined by the following expression:

$$\Psi(\eta, \gamma, z_0) = \frac{\varphi\left(\frac{1}{\gamma}, z_0\right) K\left(\frac{1}{\eta}, z_0\right) + \varphi\left(\frac{1}{\eta}, z_0\right) K\left(\frac{1}{\gamma}, z_0\right)}{\eta + \gamma} - \frac{\chi\left(\frac{1}{\gamma}, z_0\right) L\left(\frac{1}{\eta}, z_0\right) + \chi\left(\frac{1}{\eta}, z_0\right) L\left(\frac{1}{\gamma}, z_0\right)}{\eta + \gamma} + \frac{M\left(\frac{1}{\eta}, z_0\right) M\left(\frac{1}{\gamma}, z_0\right) - N\left(\frac{1}{\eta}, z_0\right) N\left(\frac{1}{\gamma}, z_0\right)}{\eta + \gamma} - \Phi(\eta, \gamma, z_0) - R_0(\eta, \gamma, y_0), \qquad (11)$$

[Expressions for functions $\Phi(\eta, \gamma, z_0)$ and $R_0(\eta, \gamma, z_0)$ are listed in refs. 1 and 2.] The functions $K(x, z_0) = \psi(0, 1/x, z_0)$ and $L(x, z_0) = \psi(z_0, 1/x, z_0)$ with $(x = 1/\gamma)$, satisfy the following set of equations (in the q-approximation):

$$K(x, z_0) = 1 + \frac{q}{2} x \int_0^1 \frac{M(x, z_0) M(y, z_0) - N(x, z_0) N(y, z_0)}{x + y}\, dy + \frac{q}{2} x \int_0^1 \frac{\varphi(x, z_0) K(y, z_0) + \varphi(y, z_0) K(x, z_0) - \chi(y, z_0) L(x, z_0) - \chi(x, z_0) L(y, z_0)}{x + y}\, dy; \qquad (12a)$$

$$L(x, z_0) = e^{-\frac{z_0}{x}} + \frac{q}{2} x \int_0^1 \frac{M(x, z_0) N(y, z_0) - N(x, z_0) M(y, z_0)}{y - x}\, dy + \frac{q}{2} x \int_0^1 \frac{\varphi(x, z_0) L(y, z_0) - \varphi(y, z_0) L(x, z_0) + \chi(y, z_0) K(x, z_0) - \chi(x, z_0) K(y, z_0)}{y - x}\, dy. \qquad (12b)$$

≤ 0.4, $K(x, z_0) = 3\varphi(x, z_0) - 2$, $L(x, z_0) = 3\chi(x, z_0) - z_0/x$.

In the spectral range where reabsorption is negligi- the average true fluorescence lifetime in the crystal, al to $T^{(\nu)}_{0,d}(\gamma) = \Psi(0, \gamma, z_0)/\Phi(0, \gamma, z_0)$, is determined by following basic formula:

$$\tau(\gamma) = T^{(\nu)}_d(\tau) = \overline{T}(\tau) = \frac{\frac{K(x, z_0) - L'(x, z_0)}{\varphi(x, z_0) - \chi(x, z_0)} + \frac{K(\infty, z_0)}{\varphi(\infty, z_0)} - 1}{\tau(\gamma)} - \frac{\frac{M(\infty, z_0)}{\varphi(\infty, z_0)}\left(\frac{M(\infty, z_0)}{\varphi(\infty, z_0)} - 1\right)}{\tau(\gamma)} + \frac{M(\infty, z_0)}{\varphi(\infty, z_0)} - 1. \qquad (13)$$

function $\overline{\tau}(\gamma)$ in this case is defined by the expres- n:

$$\tau(\gamma) = \frac{M(x, z_0) - N(x, z_0)}{\varphi(x, z_0) - \chi(x, z_0)} + \frac{M(\infty, z_0)}{\varphi(\infty, z_0)} - 1, \qquad (14)$$

ained in ref. 1. The functions $\varphi(x, z_0)$, $\chi(x, z_0)$, $z_0)$, $N(x, z_0)$ are known functions (see refs. 1 and 2).

It is easy to calculate the true fluorescence lifetime from Eq. (13), provided one has a table of values of the functions $K(x, z_0)$ and $L(x, z_0)$.

The functions $K(x, z_0)$ and $L(x, z_0)$ were not calculated in the present paper. In case of an infinitely large z_0, the function $L(x, z_0) = 0$, and $K(x, z_0)$ is transformed into the function $K(x)$, which is defined by

$$K(x) = 1 + \frac{q}{2} x \int_0^1 \frac{M(x) M(y)}{x + y}\, dy + \frac{q}{2} x \int_0^1 \frac{\varphi(y) K(x) + \varphi(x) K(y)}{x + y}\, dy. \qquad (15)$$

Introducing the definitions $\theta(x) = M(x)/\varphi(x)$, $\omega(x) = K(x)/\varphi(x)$, and using the equations for $\varphi(x)$ and $M(x)$ and Eqs. (49) and (51) from ref. 1, Eq. (15) can be written in the following form:

$$\omega(x) = 1 + \theta^2(x) - \theta(x) + \frac{q}{2} x\varphi(x) \int_0^1 \frac{\omega(y)\varphi(y)\,dy}{x+y}. \qquad (16)$$

This last equation was obtained and investigated in ref. 3. The same paper gives tables of values of the function $\omega(x)$. It is not very difficult to compile tables of values of the function K(x) since very good tables of $\varphi(x)$ are available (see ref. 4). We will consider the function K(x) as known. As we will show below, an asymptotic expression can be obtained for the functions $K(x, z_0)$ and $L(x, z_0)$ at large z_0. Knowing $\varphi(x)$, M(x), and K(x), values of $K(x, z_0)$ and $L(x, z_0)$ can be calculated for large values of z_0 ($z_0 \gg 1$) with good accuracy, so that the true fluorescence lifetime of the crystal can be obtained.

Equations satisfying the functions $K(x, z_0)$ and $L(x, z_0)$ can be found by a method described in detail in ref. 2:

$$K(x, z_0) = 1 + \frac{q}{2}\int_0^1 \frac{dy}{y}\int_0^{z_0} e^{-(z_0-z)\left(\frac{1}{x}+\frac{1}{y}\right)} [\varphi(x, z)K(y, z) + \varphi(y, z)K(x, z) + M(x, z)M(y, z)]\,dz; \qquad (17)$$

$$L(x, z_0) = e^{-\frac{z_0}{x}} + \frac{q}{2}\int_0^1 \frac{dy}{y}\int_0^{z_0} e^{-\frac{z_0-z}{x}} [\varphi(x, z)L(y, z) + \chi(y, z)K(x, z) + M(x, z)N(y, z)]\,dz. \qquad (18)$$

As far as we know, Eqs. (17) and (18) are new expressions.

Let us examine Eqs. (17) and (18), assuming that $z_0 \gg 1$. We will search for an asymptotic expression of the function $K(x, z_0)$ in the form

$$K(x, z_0) = K(x) - k(x) z_0^2 e^{-2kz_0}, \qquad (19)$$

where k is a constant, determined by the equation

$$\frac{q}{2k} \ln \frac{1+k}{1-k} = 1 \qquad (20)$$

or by an equivalent equation (see ref. 5 which contains a table of values of k for various q):

$$\frac{q}{2}\int_0^1 \frac{\varphi(y)}{1-ky}\,dy = 1. \qquad (21)$$

If we introduce (19) the asymptotic expressions for functions $\varphi(x, z_0)$, $\chi(x, z_0)$, $M(x, z_0)$, and $N(x, z_0)$ given in ref. 2 will have the form

$$\varphi(x, z_0) = \varphi(x) - C\frac{x\cdot\varphi(x)}{1-kx} e^{-2kz_0}, \qquad (22)$$

$$\chi(x, z_0) = C_1 \frac{x}{1-kx}\cdot\varphi(x) e^{-kz_0}, \qquad (23)$$

$$M(x, z_0) = M(x) - D\frac{x\varphi(x)}{1-kx} z_0 e^{-2kz_0}, \qquad (24)$$

$$N(x, z_0) = D_1 \frac{x}{1-kx}\varphi(x) e^{-kz_0}, \qquad (25)$$

where C, C_1, D, and D_1 are known constants [see ref. 2 and Eq. (17)].

Discarding terms of order lower than $z_0^2 e^{-2kz_0}$ and using Eq. (15), we will find that Eq. (17) is satisfied by a solution of the form

$$K(x, z_0) = K(x) - E\cdot\frac{x}{1-kx}\varphi(x)\cdot z_0^2 e^{-2kz_0}. \qquad (26)$$

Similarly, Eq. (18) will give an asymptotic expression for the function $L(x, z_0)$

$$L(x, z_0) = E_1 \frac{x\varphi(x)}{1-kx} z_0^2 e^{-kz_0}.$$

In Eqs. (26) and (27), E and E_1 are constants which we will find below by the method used to find D and D_1 in ref. 2.

To do this, let us first represent Eqs. (12a) and (12 for $x = 1/m$, $m < 1$ in the following form:

$$K\left(\frac{1}{m}, z_0\right) = \frac{D_K\left(\frac{1}{m}, z_0\right)}{D\left(\frac{1}{m}, z_0\right)}, \quad L\left(\frac{1}{m}, z_0\right) = \frac{D_L\left(\frac{1}{m}, z_0\right)}{D\left(\frac{1}{m}, z_0\right)}.$$

Where $D_K(1/m, z_0)$, $D_L(1/m, z_0)$ are determinants for which expressions can be easily derived from Eqs. (12 and (12b). We will not list them here because of the bulkiness of the expressions obtained. It was shown in ref. 6 that

$$D\left(\frac{1}{m}, z_0\right) = 1 - \frac{q}{2m} \ln \frac{1+m}{1-m}.$$

It follows from Eq. (29) that for $m = k$, $D(1/k, z_0) = 0$. By virtue of this, two conditions are fulfilled for $m = k$:

$$D_K\left(\frac{1}{k}, z_0\right) = 0, \quad D_L\left(\frac{1}{k}, z_0\right) = 0.$$

It can be demonstrated that, by using the similar relationships for the determinants D_M, D_L, D_φ, D_χ obtained in ref. 2, the two equations given in (30) are reduced to a single relationship of the form

$$\left[e^{-kz_0}\frac{q}{2}\int_0^1 \frac{K(y, z_0)}{1+ky}\,dy + \frac{q}{2}\int_0^1 \frac{L(y, z_0)}{1-ky}\,dy\right] = \frac{\chi\left(\frac{1}{k}, z_0\right)}{\varphi\left(\frac{1}{k}, z_0\right)}\left[\frac{q}{2}\int_0^1 \frac{K(y, z_0)}{1-ky}\,dy + e^{-kz_0}\frac{q}{2}\int_0^1 \frac{L(y, z_0)}{1+ky}\,dy\right] + \left(\frac{N\left(\frac{1}{k}, z_0\right)\varphi\left(\frac{1}{k}, z_0\right) - M\left(\frac{1}{k}, z_0\right)\chi\left(\frac{1}{k}, z_0\right)}{\varphi^2\left(\frac{1}{k}, z_0\right)}\right) \times \left[\frac{q}{2}\int_0^1 \frac{M(y, z_0)}{1-ky}\,dy + e^{-kz_0}\cdot\frac{q}{2}\int_0^1 \frac{N(y, z_0)}{1+ky}\,dy\right],$$

In order to take advantage of this relationship to d termine one of the unknown constants, it is necessary t calculate the expression

$$\lim_{m\to k} \frac{N\left(\frac{1}{m}, z_0\right)\varphi\left(\frac{1}{m}, z_0\right) - M\left(\frac{1}{m}, z_0\right)\chi\left(\frac{1}{m}, z_0\right)}{\varphi^2\left(\frac{1}{m}, z_0\right)} = \lim_{m\to k} \frac{D_N\left(\frac{1}{m}, z_0\right)D_\varphi\left(\frac{1}{m}, z_0\right) - D_M\left(\frac{1}{m}, z_0\right)D_\chi\left(\frac{1}{m}, z_0\right)}{D_\varphi^2\left(\frac{1}{m}, z_0\right)}.$$

Expanding all values entering into this expression as a power series in the difference $m - k$, restricting ourselves to the first term of the expansion and noting that $D_\varphi = 0$ and $D_\chi = 0$, we find, after a simple but rath lengthy calculation which we will omit here, that

$$\lim_{m\to k}\frac{N\left(\frac{1}{m},\ z_0\right)\varphi\left(\frac{1}{m},\ z_0\right)-M\left(\frac{1}{m},\ z_0\right)\chi\left(\frac{1}{m},\ z_0\right)}{\varphi^2\left(\frac{1}{m},\ z_0\right)}$$

$$\simeq\frac{1}{2}z_0^2C_1\varphi\left(\frac{1}{k}\right)\frac{q}{2}\int_0^1\frac{\varphi(x)\,x\,dx}{(1-kx)^2}\,. \qquad (32)$$

Substituting expressions (24)-(27) into Eq. (31), and arding all terms of the form $z_0^2e^{-kz_0}$ except the est ones, we find that the constant E_1 is equal to

$$E_1=\frac{1}{2}\varphi^2\left(\frac{1}{k}\right)\cdot C_1. \qquad (33)$$

We will use the following equation to determine the nd constant:

$$\chi(z_0)=\frac{q}{2}+\frac{1}{2}\left(M_0^2(z_0)-N_0^2(z_0)\right)+\varphi_0(z_0)K_0(z_0)-\chi_0(z_0)L_0(z_0), \qquad (34)$$

s equation is easy to obtain by multiplying by q/2, grating both sides of Eq. (12a) with respect to x from 1, and going through calculations similar to those ormed to obtain analogous relationships for the functions φ, χ, M, and N.

$K_0(z_0)$, $L_0(z_0)$, $M_0(z_0)$, $N_0(z_0)$, $\varphi_0(z_0)$, and $\chi_0(z_0)$ in (34) must be considered as momenta of the functions $z_0)$, $L_0(x, z_0)$, $M_0(x, z_0)$, $N_0(x, z_0)$, $\varphi_0(x, z_0)$, and $z_0)$, defined for an arbitrary function f(x) as follows:

$$f_m=\frac{q}{2}\int_0^1 f(x)\,x^m\,dx. \qquad (35)$$

Using Eqs. (22)-(27) to calculate the momenta of functions φ, χ, M, N, K, and L entering into relation (34), we find that

$$kE=D_1^2. \qquad (36)$$

In this calculation, we used the relationship

$$K_0(\infty)=\frac{q}{2}+\frac{1}{2}M_0^2(\infty)+\varphi_0(\infty)K_0(\infty). \qquad (37)$$

which is easily obtained from Eq. (15) by the method indicated above.

Equations (33) and (36) thus define the desired constants E and E_1 in terms of the known constants C and D_1.*

*It should be noted that the average fluorescence lifetime of the crystal is calculated in ref. 7 with the help of approximate relations for the functions $\varphi(x, z_0)$ and $\chi(x, z_0)$ [these functions are designated in ref. 7 as $\varphi(x)$ and $\psi(x)$ respectively], obtained for arbitrary q and z_0. However, the asymptote of these functions for $z_0 \gg 1$ does not coincide with expressions (22) and (23) obtained in ref. 6 on the basis of a solution of exact equations.

Since the results of the present paper are based on the results of ref. 6, they are also different from the results of ref. 7.

We cannot perform a more quantitative comparison at this time, however, as this would unduly lengthen the paper.

(b) When calculating the limiting values of the fluorescence lifetime for frequencies of light weakly absorbed by the crystal (large $x = 1/\gamma$, $\gamma = k/kc$), it is interesting to find the value of

$$T(x=\infty)=\lim_{x\to\infty}\frac{\frac{K(x,\ z_0)-L(x,\ z_0)}{\varphi(x,\ z_0)-\chi(x,\ z_0)}+\frac{K(\infty,\ z_0)}{\varphi(\infty,\ z_0)}-\frac{M(\infty,\ z_0)}{\varphi(\infty,\ z_0)}\left(\frac{M(\infty,\ z_0)}{\varphi(\infty,\ z_0)}-1\right)-1}{\bar{\tau}(x)}+\frac{M(\infty,\ z_0)}{\varphi(\infty,\ z_0)}-1, \qquad (38)$$

e for $x = \infty$, $K(\infty, z_0) = L(\infty, z_0)$ and $\varphi(\infty, z_0) = \chi(\infty, z_0)$. Let us find asymptotic expressions for the functions $z_0)$ and $L(x, z_0)$ at large values of x. To do this, it ecessary to assume in Eqs. (28) that $1/m = x$, $m < 1$ to expand $D_K(x, z_0)$, $D_L(x, z_0)$, and $D(x, z_0)$ as a series in powers of $1/x \ll 1$, restricting oneself to the first term of the expansion. Let us list the result of a simple, but cumbersome calculation of the desired asymptotic relations for the functions $K(x, z_0)$ and $L(x, z_0)$ for large x:

$$K(x,\ z_0)=\varphi(x,\ z_0)\left\{1+\frac{K_0(1-\varphi_0)+L_0\chi_0}{1-q}-\frac{1}{(1-q)\,x}[K_1(1-\varphi_0)+K_0\varphi_1\right.$$
$$\left.+L_0\chi_1-L_1\chi_0]\right\}-\chi(x,\ z_0)\left\{\frac{L_0(1-\varphi_0)+K_0\chi_0}{1-q}-\frac{1}{x(1-q)}[L_1(1-\varphi_0)+L_0\varphi_1\right.$$
$$\left.+K_0\chi_1-K_1\chi_0]\right\}+M(x,\ z_0)\left\{\frac{M_0(1-\varphi_0)+N_0\chi_0}{1-q}-\frac{1}{x(1-q)}[M_1(1-\varphi_0)+M_0\varphi_1\right.$$
$$\left.+N_0\chi_1-N_1\chi_0]\right\}-N(x,\ z_0)\left\{\frac{N_0(1-\varphi_0)+M_0\chi_0}{1-q}-\frac{1}{x(1-q)}[N_1(1-\varphi_0)+N_0\varphi_1+M_0\chi_1-M_1\chi_0]\right\}; \qquad (39)$$

$$L(x,\ z_0)=\chi(x,\ z_0)\left\{1+\frac{K_0(1-\varphi_0)+L_0\chi_0}{1-q}+\frac{1}{x(1-q)}[K_1(1-\varphi_0)+K_0\varphi_1\right.$$
$$\left.+L_0\chi_1-L_1\chi_0]\right\}-\varphi(x,\ z_0)\left\{\frac{L_0(1-\varphi_0)+K_0\chi_0}{1-q}+\frac{1}{x(1-q)}[L_1(1-\varphi_0)+L_0\varphi_1\right.$$
$$\left.+K_0\chi_1-K_1\chi_0]\right\}+N(x,\ z_0)\left\{\frac{M_0(1-\varphi_0)+N_0\chi_0}{1-q}+\frac{1}{x(1-q)}[M_1(1-\varphi_0)+M_0\varphi_1\right.$$
$$\left.+N_0\chi_1-N_1\chi_0]\right\}-M(x,\ z_0)\left\{\frac{N_0(1-\varphi_0)+M_0\chi_0}{1-q}+\frac{1}{x(1-q)}[N_1(1-\varphi_0)+N_0\varphi_1+M_0\chi_1-M_1\chi_0]\right\}. \qquad (40)$$

For the sake of brevity, we omitted the argument z_0 in the momenta of the functions M, N, φ, χ, K, and L.

It follows from Eqs. (39) and (40), in view of Eq. (34), that

$$K(\infty, z_0) = L(\infty, z_0) = 1 + \frac{q + M_0^2 - N_0^2}{2(1-q)} - \frac{L_0(1-\varphi_0) + K_0\chi_0}{1-q} + \frac{M(\infty, z_0)}{\varphi(\infty, z_0)}\left[\frac{q}{2(1-q)} - \frac{N_0(1-\varphi_0) + M_0\chi_0}{1-q}\right]. \quad (41)$$

Taking advantage of expressions (39), (40), and of asymptotic expressions for functions $\varphi(x, z_0)$, $\chi(x, z_0)$, $M(x, z_0)$, $N(x, z_0)$ for large x, obtained in ref. 2, we find that

$$\bar{T}(x=\infty) = \frac{1}{1-q} - \frac{\left(\frac{M(\infty, z_0)}{\varphi(\infty, z_0)} - 1\right) f(M, N) + f(K, L)}{\varepsilon(x=\infty)}, \quad (42)$$

where f(g, h) is a functional of integrated functions g(x) and h(x) which is determined by the formula

$$f(g, h) = \frac{2\varphi(\infty, z_0)[g_1 - h_1 + \varphi(\infty, z_0)(g_0 - h_0)(\varphi_1(z_0) - \chi_1(z_0))]}{z_0 - 2\varphi(\infty, z_0)(\varphi_1(z_0) - \chi_1(z_0))}, \quad (43)$$

and $\bar{\tau}(x=\infty)$ is a known quantity (see ref. 2). Formula (43) is valid for any z_0. It follows from Eq. (42) that for $z_0 \to \infty$, $\bar{T}(x=\infty) \to 1/(1-q)$.

It should be mentioned that it is inconvenient to use formula (42) to calculate the value of $\bar{T}(x=\infty)$ at small z_0, because it is then necessary to know the values of functions $M(x, z_0)$, $N(x, z_0)$, $K(x, z_0)$, and $L(x, z_0)$ with very great accuracy. In order to get around this difficulty, let us find an approximate expression for the average true time at small thicknesses of the crystal, such that $z_0 \ll 1$.

Let us first of all note that it follows from formulas (9) and (11) that

$$\frac{q}{2}\int_0^1 dy \int_0^{z_0} \psi\left(z, \frac{1}{y}, z_0\right) dy = \frac{q}{2}\int_0^1 \Psi\left(0, \frac{1}{y}, z_0\right) dy$$

$$= \varphi(\infty, z_0)[K_1(z_0) - L_1(z_0) + (K_0(z_0) - L_0(z_0))(\varphi_1(z_0)$$

$$- \chi_1(z_0))\varphi(\infty, z_0)] + \left(\frac{M(\infty, z_0)}{\varphi(\infty, z_0)} - 1\right)[(M_1(z_0) - N_1(z_0)$$

$$+ (M_0(z_0) - N_0(z_0))(\varphi_1(z_0) - \chi_1(z_0))\varphi(\infty, z_0)]. \quad (44)$$

If $z_0 \ll 1$, the left side of Eq. (44) can be written as follows, as an approximation:

$$\frac{q}{2}\int_0^1 dy \int_0^{z_0} \varphi\left(z, \frac{1}{y}, z_0\right) dz = \frac{q}{2}\int_0^1 dy z_0 \frac{1}{2}\left(\psi\left(0, \frac{1}{y}, z_0\right) + \psi\left(z_0, \frac{1}{y}, z_0\right)\right) = \frac{z_0}{2}(K_0(z_0) + L_0(z_0)).$$

Substituting Eq. (43) in (42) and making use of Eqs. (44) and (45), we find that

$$\bar{T}(x=\infty) = \frac{1}{1-q} - \frac{K_0(z_0) + L_0(z_0)}{\varphi(\infty, z_0) - M_0(z_0) - N_0(z_0)}. \quad (4$$

Like the average "exponential" time, $\bar{T}(x=\infty)$ ten toward unity at the limit $z_0 \to 0$, because in that case $M_0(z_0) \to q/2$, $K_0(z_0) \to q/2$, $N_0(z_0) \to q/2$, $L_0(z_0) \to q/2$, $\varphi(\infty, z_0) \to 1$. This is a reflection of the fact that reabsorption is unimportant in infinitely thin crystal plates.

These results can be used in the theory of radiant energy transfer in stellar atmospheres to calculate the average lifetime of quanta in a medium and in the calculation of a nonstationary radiation field.

In conclusion, the author would like to cordially thank V. M. Agranovich for suggesting the problem, and for his constant interest and valuable advice.

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THE TRANSPARENCY OF CaF_2, SrF_2, AND BaF_2 CRYSTALS AND THE EFFECT OF HARD RADIATION ON THEM

E. G. Chernevskaya (pp. 513-517)

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The transmission of synthetic CaF_2, SrF_2, and BaF_2 single crystals was studied in the range from 0.13 to 13 μ. The effect of γ-radiation on these crystals was also studied. It was discovered that the absorption in the vacuum region of the spectrum has a dual nature in CaF_2 and SrF_2 synthetic crystals; the visible coloration of SrF_2 and of irradiated CaF_2 crystals is related to their transparency in this part of the spectrum. SrF_2 and BaF_2 crystals are more resistant to the effect of hard radiation than CaF_2 crystals, and green SrF_2 crystals are discolored by γ-irradiation.

Synthetic single crystals of alkaline earth metal ...ides—fluorite (CaF_2) and its analogues (SrF_2 and ...)—offer considerable interest as optical media with ...ries of particular optical properties (high trans...ncy in a large range of wavelengths, small scatter...n the visible region, etc.[1-4]).

A previously published paper[4] contained a preliminary communication about the growing of optical strontium and barium fluoride single crystals. Measured ...s of optical constants and a general spectral ab...tion curve of the first grown crystal specimens ... also given. A more detailed study of the transmission spectra of single crystals is made in the present ..., particular attention being given to strontium fluoride crystals, for which literature data were missing. ...lso investigated the coloration developed in crys...by the action of hard radiation.

Single crystals of alkaline earth metal fluorides ... grown from synthetic compounds of a high degree ...rity with addition of lead fluoride and of graphite ...,[4] Lead fluoride and graphite were added to the ...ure in order to create reducing conditions and to ...ate the melt with fluorine ions.

Measurements of crystal absorption were made in ...isible spectral range with a Beckman type spectro...meter, in the Schumann region with an SP-41 spec...notometer, and in the infrared with an IKS-11 instru...; the specimens were 5 mm thick.

TRANSMISSION SPECTRA OF MeF_2 SINGLE CRYSTALS

According to the literature,[3] synthetic calcium fluoride crystals are frequently colored red-violet and they ...paque in the spectral range with wavelengths shorter ... 210 mμ. The synthetic calcium and barium fluoride ...tals which we obtained were colorless and had a high ...niform transmission in the visible part of the spec... The investigation of calcium fluoride crystals in ...chumann region of the spectrum revealed the exis... of two types of crystals. Some crystals are trans...mt down to 140-135 mμ, transmitting in this region ...oximately 20-40% of the light. The transparency of ... specimens corresponds to the transparency of cal... fluoride crystals obtained by other authors; the ...smission of these crystals drops sharply in the in...al 230-210 mμ, and the threshold of transmission is ...ed at about 200 mμ (Fig. 1, curves 3 and 4).

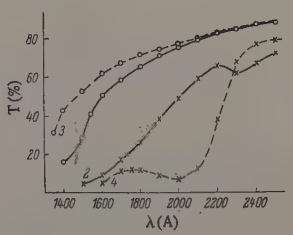

Fig. 1. Transmission of ultraviolet radiation by CaF_2 and SrF_2 crystals. Curve 1—SrF_2 ("yellow"); curve 2—SrF_2 (green); curve 3—CaF_2 (colorless, colored blue after γ-irradiation); curve 4—CaF_2 (colorless, colored purple after γ-irradiation).

Single crystals of strontium fluoride which we had grown were, as a rule, colored during the growing process. Two types of coloration were hereby representative: a pale yellow, noticeable only in a thick layer, and a bright green. The "yellow" specimens of strontium fluoride have a uniform transmission in the whole visible range of the spectrum and they do not show any apparent absorption bands (Fig. 2, curve 5).

Green strontium fluoride crystals are characterized by a larger general light absorption and they have several clearly defined bands. The absorption spectrum (Fig. 2, curve 1) consists of an intense and relatively narrow band with a maximum around 450 mμ and of two less intense bands located in the 630 and 295 mμ regions. The curve has still another weak absorption band near 230 mμ in the short wavelength part of the spectrum.

"Yellow" SrF_2 crystals are more transparent in the 250 to 135 mμ region than crystals colored green; the short wavelength transmission edge of "yellow" specimens is at about 150 mμ, and they transmit up to 20-30% of the light in this spectral range (Fig. 1, curves 1 and 2). It is possible that the centers which cause the green coloration of SrF_2 crystals also determine the short wavelength absorption of the crystals.

No differences in the type of transmission in the ultraviolet were observed for barium fluoride crystals. The short wavelength transmission edge of BaF_2 crystals is located at about 160 mμ. It must be mentioned that strontium fluoride and calcium fluoride crystals having poor light transmission in the ultraviolet were, as a rule, grown under bad vacuum conditions.

CaF_2, SrF_2, and BaF_2 crystals have fairly well-defined limits of transmission in the infrared range of the

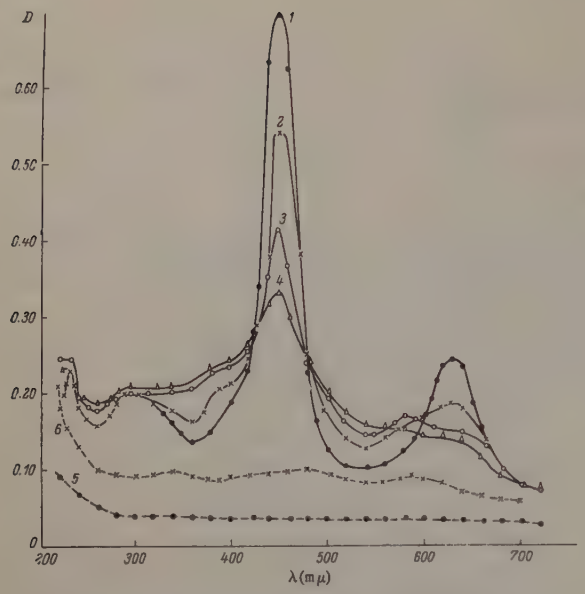

Fig. 2. Absorption spectra of green (I) and "yellow" (II) SrF_2 crystals before and after γ-irradiation. Curve 1—crystal I before γ-irradiation; curve 2—crystal I after γ-irradiation with a dose of 1.58×10^6 roentgens (bright green color); curve 3—crystal I after γ-irradiation with 6.63×10^6 roentgens (pale green color); curve 4—crystal I after γ-irradiation with 3.5×10^7 roentgens ("yellow" color); curve 5—crystal II before γ-irradiation; curve 6—crystal II after γ-irradiation with 3.5×10^7 roentgens. For $\lambda < 320$ mμ the points on curve 1 coincide with the points (crosses) of curve 2.

spectrum: CaF_2 samples transmit up to 50% in the region around 9.4 μ, while SrF_2 has this transmission around 11 μ and BaF_2 around 12.3 μ.

EFFECT OF γ-IRRADIATION ON MeF_2 SINGLE CRYSTALS

Crystals of alkaline earth metal fluorides (like the much more thoroughly investigated alkali-halide crystals) are susceptible to coloration by the action of short wavelength ultraviolet radiation as well as by the action of x-rays and radioactivity radiations. The largest number of references deals with color centers in fluorite crystals.[2,3,5-7] Absorption bands in the spectra of these crystals are located somewhat differently according to the data of different authors, but in all cases they remain in the same spectral regions. The absorption spectrum of colored BaF_2 crystals is described in ref. 2. Color centers formed during the coloration of fluorite crystals were identified in ref. 5 as complex electronic centers (F_2 centers).

In our investigations crystals of CaF_2, SrF_2, and BaF_2 were exposed to γ-rays (Co^{60}).* Specimens of synthetic fluorite (CaF_2) acquired a purple or a blue colo tion as a result of irradiation. Absorption curves of crystals colored blue or purple are shown in Fig. 3. absorption curve of purple crystals has two bands of most equal intensity with maxima near 520 and 375 m and a weak band near 330 mμ. The long wave absorpti band is considerably displaced to shorter wavelengths as compared to data by other authors. An absorption spectrum similar to ours was observed in additively colored calcium fluoride crystals in the work reporte in ref. 6.

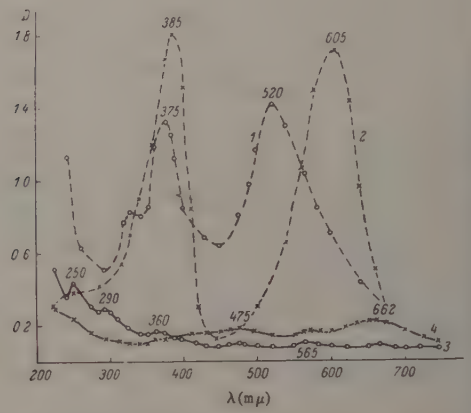

Fig. 3. Absorption spectra of CaF_2 and BaF_2 crystals after a γ-irradiation dose of 7.5×10^4 roentgens. Curve 1—CaF_2 (purple); curve 2—CaF_2 (blue); curve 3—BaF_2 (yellowish); curve 4—BaF_2 (pale blue). CaF_2 and BaF_2 are colorless before irradiation.

The absorption spectrum of blue CaF_2 crystals, that of the purple crystals, consists of two intense ba whose maxima are located at approximately 605 and mμ, and of a weak band at 260 mμ. Blue coloration w previously observed on natural fluorite crystals expo to γ-irradiation[7] and in additively colored crystals.[6] absorption curve which we obtained is closest to the of ref. 7.

It follows from our observations that the type of oration of synthetic CaF_2 crystals appearing on γ-irr ation is closely related to the transparency of the cry tals in the Schumann region. Blue color is acquired crystals transparent down to 140-135 mμ. Crystals h a short wavelength transmission edge at 200 mμ beco colored purple. Apparently there are two kinds of ce ters in colored calcium fluoride and in nonirradiated SrF_2 crystals, namely, centers causing a purple colo and centers producing blue coloration, which, possibl in some manner determine the short wavelength abso tion of synthetic calcium fluoride crystals. Further i vestigations are needed to clarify the relationship be tween absorption in the ultraviolet region and the typ of coloration of irradiated CaF_2 crystals.

Crystals of barium fluoride are considerably mo resistant than fluorite crystals to the effect of hard r diation: the crystals acquire a pale blue or a pale ye coloration upon γ-irradiation with 7.5×10^4 or more roentgens (see Fig. 3). The absorption spectrum of lowish colored crystals is close to the spectrum of x-rayed BaF_2 crystals described in ref. 2.

*The author wishes to take advantage of this opportunity to express her sincere gratitude to N. V. Berbash for making possible the irradiation of the crystals.

The effect of γ-radiation on strontium fluoride sin-crystals proved to be very different and peculiar. ow colored SrF_2 crystals do not change color upon diation with 7.5×10^7 roentgens and they are charac-ed by a small increase in the intensity of coloration, h remains apparent only in a thick layer. The ab-tion curve of such samples irradiated with 3.5×10^7 tgens (dose rate of 1×10^4 r/hr), has weak maxima ae region of 340, 470-480, and 590 mμ (Fig. 2, curve Green-colored SrF_2 single crystals are gradually dis-red by lengthy γ-irradiation.

Absorption spectra of a SrF_2 crystals, colored green ng its growing process and later exposed to the ac-of γ-rays for variable lengths of time, are shown in 2 (curves 2, 3, 4). The general character of the ab-tion curve is conserved when the duration of irradia-is increased, but the intensity of individual absorption ls is substantially changed. The highest and most nar-band with a maximum near 450 mμ is gradually de-sed and its intensity drops to one half after irradia-with 3.5×10^7 roentgens. The long wavelength band a maximum at 632 mμ suffers a similar drop. In the t wavelength part of the spectrum the band with a mum around 295 mμ remains basically unchanged only its long wavelength part is noticeably raised. he other hand, two additional bands with maxima nd 390 and 580 mμ appear in the absorption spec-n of SrF_2 crystals after fairly strong irradiation (of oximately 1.5×10^6 roentgens).

Let us point out that the "yellow" coloration of ntium fluoride crystals soon reaches its saturation that the intensity of the absorption bands remains practically unchanged after lengthy γ-irradiation. Barium fluoride crystals behave in a similar manner. Synthetic CaF_2 crystals are most sensitive to the action of hard radiation; as was shown above, the CaF_2 crystals acquire coloration after even a small dose of radiation, the intensity of coloration increasing rapidly with an increase in the dose.

Of all three crystals of alkaline earth metal fluorides the strontium fluoride single crystals thus appear to be the most resistant to the action of hard radiation.

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INVESTIGATION OF THE EFFECT OF A FLUX ON ACTIVATOR CONCENTRATION IN A PHOSPHOR BY THE PARAMAGNETIC ABSORPTION METHOD

V. G. Dubinin (pp. 518-522)

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A study is made of the effect of a flux on the penetration of divalent and trivalent activators into the divalent SrS lattice. It is shown that the concentration of Eu^{2+} increases when any kind of flux is introduced. In the case of Gd^{3+}, the introduction of flux may result in either an increase or a decrease of the activator concentration, depending on the nature of the flux, in accordance with the principle of charge compensation.

It has been shown[1] that phosphors prepared with and out flux under identical conditions differ not only in concentration of the activator entering the lattice ng baking, but also in a number of optical properties. se include brightness during excitation, the law of nescence decay, the magnitude of the emitted light ., etc.) Reference 1 gives the results of a study of the ct of $SrCl_2$ and LiF fluxes on activator concentration ie SrS:Eu,Sm phosphor.

The action of a flux, i.e., its effect on the activator on the properties of the phosphor as a whole, has so been studied only to a small extent, although it is of rest in connection with the luminescence of crystal-phosphors. We have therefore carried out a more iled investigation in this direction, based on the use ae paramagnetic absorption method. We studied the entration of the activator in the host lattice as a tion of the amount of flux introduced into the batch, as well as the effect of the flux on other activators which were used in preparing the phosphor but are also independently capable of paramagnetic absorption.

To solve the first problem, we prepared phosphors with different amounts of $SrCl_2$ flux.* The following amounts of $SrCl_2$ were used for a 10 gm batch: 0, 0.9, 1.8, and 3.6 gm. (The standard amount is 1.8 gm $SrCl_2$.) The quantities of phosphor in the tubes were chosen so as to contain equal amounts of activator. As in the preceding communication,[1] the signal of the paramagnetic absorption of different samples was compared with the intensity of the absorption line of a copper sulfate single crystal mounted on the end of the resonator cavity.

*As indicated in ref. 1, for this particular flux it is possible to determine portions containing identical amounts of activator added by weighing before and after baking.

In order to eliminate errors connected with the possibility of a variation in the position of the test tubes in the resonator during different measurements (in spite of a special mounting), the absorption spectrum was recorded many times, after which an average value was found.

Table 1 contains the data on the variation of activator concentration as a function of the amount of flux added to the batch. The concentrations were determined from the relative intensities of the lines in the paramagnetic absorption spectrum of Eu^{++}. It is easily seen that a flux content which is half the standard amount (i.e., 0.9 gm for a 10 gm batch) changes the amount of activator entering the host lattice by almost the same factor. However, a larger amount of flux apparently affects also the host lattice as well, since the phosphor then changes markedly in color and external appearance, forming a brownish vitreous mass. In this case, the activator concentration is reduced, which may possibly be caused by partial destruction of the SrS lattice.

Table 1. Activator Concentration as a Function of the Amount of Flux Introduced into the Batch

Phosphor	Flux	Amount of flux (gm) per 10 gm of batch	Quantity of phosphor in sample (gm)*	Activator concentration referred to phosphor without flux**	Brightness during excitation (rel. units)	n (%)***
SrS-Eu, Sm	—	—	0.153	100	60	~5
SrS-Eu, Sm	$SrCl_2$	0.9	1.168	140	78	~2
SrS-Eu, Sm	$SrCl_2$	1.8	0.180	150	80	~2
SrS-Eu, Sm	$SrCl_2$	3.6	0.213	110	39	~1

*The portions were chosen so as to give equal amounts of the activator, and were determined by weighing the phosphor after baking.

**Measurements accurate to within 10%.

***Magnitude of the emitted light sum (in relative units) which is equal to the ratio number of the quanta emitted to the number of activator ions computed for the given sample.

A direct measurement of the width of the Eu^{2+} paramagnetic absorption lines did not show any differences between phosphors containing large and small amounts of flux. This indicates that even a large amount of flux added to the batch has no direct influence on the paramagnetic Eu^{2+} ion. However, as seen in Table 1, different amounts of added flux affect the steady state phosphor brightness, the magnitude of the light sum, and the activator concentration.

In the SrS:Eu,Sm phosphor the electronic paramagnetic resonance method makes it possible to follow the change in concentration of only one activator, Eu^{2+}, as affected by flux. The other activator, Sm^{3+}, shows paramagnetic absorption only at very low temperatures and in very high fields. It is extremely interesting, however, to follow the effect of a flux on the second trivalent ion of a two-activator phosphor, since we may assume that it will differ from the effect on a divalent ion.

In order to use this method to study the effect of flux on a two-activator phosphor, we prepared a SrS:Eu,Gd phosphor having Gd^{3+} as the second activator. This ion has the same ground state as Eu^{2+}, namely, $^8S_{7/2}$. In this case, the paramagnetic absorption spectrum consists of twelve hyperfine structure lines of Eu^{2+} and one Gd^{3+} line. When equal amounts of Eu and Gd were added to a phosphor containing flux, the Gd line was more intense than any of the Eu lines by almost a whole order of magnitude. This phosphor differs little from the SrS:Eu,Sm phosphor as regards luminescence spectra and the flash during excitation in the optical absorption band of Eu. In this case, both the Gd and the Sm exist in the lattice in the trivalent state.

By analogy with ref. 1, we prepared a series of SrS:Eu,Sm phosphors with and without the same LiF a $SrCl_2$ fluxes. The results of this experiment are show in Fig. 1 and Table 2. Figure 1 shows that the LiF flu changes the concentration of the trivalent Gd and the d valent Eu embedded in the lattice by almost the same tor. The Gd line does not appear at all in the spectrur of the phosphor with the $SrCl_2$ flux, while the relative tensity of the Eu lines is changed almost as much as f the phosphor with the LiF flux.

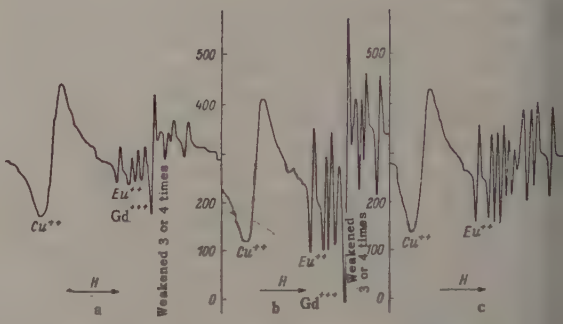

Fig. 1. Paramagnetic absorption spectra of the SrS:Eu(10^{-4}), Gd(10^{-4}) phosphor. a—Without flux; b—with LiF flux; c—with $SrCl_2$ flux. Reference standard—$CuSO_4 \cdot 5H_2O$ single crystal.

Fluxes thus have different types of effects on div lent and trivalent activators.

In order to study the effect of fluxes on a trivale ion in more detail, we prepared a series of single-ac vator phosphors, namely, SrS:Gd (10^{-4}) (without flux), SrS:Gd (10^{-4}) (LiF), and SrS:Gd (10^{-4}) ($SrCl_2$). We stu the relative concentration of Gd which entered the hos lattice due to the presence of the flux. (See Fig. 2, T 2.) It is easy to see that the results for Gd in this ca are analogous to the results shown in Fig. 1.

One might assume that the flux has a twofold effe on trivalent ions embedded in a divalent host lattice, opposed to the case of divalent ions. It not only weak the lattice, thus favoring diffusion of the activator int (as demonstrated in the case of europium), but also c ates the conditions necessary for the compensation o excess positive charge introduced by the trivalent ac vator when it replaces the cation at the nodes of the valent lattice. In the case of the LiF flux, a Gd^{3+} and pair can obviously replace two Sr^{2+} cations in the lat leaving it electrically neutral. This assumption was on the conclusions derived in ref. 2. It is shown ther the case of a ZnS phosphor, that monovalent cations

Table 2. Intensity Ratio of the Lines of the Eu^{2+} (A_{Eu}) and Gd^{3+} (A_{Gd}) Activators to the Lines of the Cu^{2+} (R_{Cu}) Reference Standard (from the Data of Figs. 1-3)

Ratio	Fig. 1			Fig. 2			Fig. 3		
	a	b	c	a	b	c	a	b	c
$\frac{A_{Eu}}{R_{Cu}}$	0.3	0.8	0.7	—	—	—	—	—	—
$\frac{A_{Gd}}{R_{Cu}}$	3.0	7.6	0.0	1.7	3.4	0.1	1.7	4.3	2.2

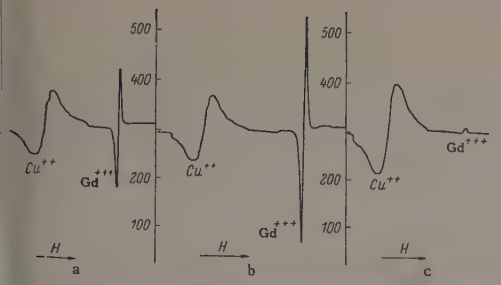

Fig. 2. Paramagnetic absorption spectra of the SrS:Gd(10^{-4}) phosphor. a—Without flux; b—with LiF flux; c—with $SrCl_2$ flux.

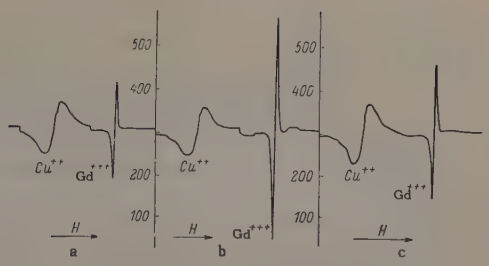

Fig. 3. Paramagnetic absorption spectra of the SrS:Gd(10^{-4}) phosphor. a—Without flux; b—with Li_2CO_3 flux; c—with Na_2CO_3 flux.

rate into a divalent lattice to an appreciable extent f there is compensation of the charge imbalance re- g from the replacement of a divalent cation by a valent one. Such a compensation may be realized simultaneous penetration of cations with a valency ling 2. It is also shown in ref. 2 that one mono- and one trivalent ion may replace two zinc ions. aper also mentions a number of patents in which it med that using Gd as the trivalent ion compen- the monovalent Ag, Au, and Cu ions leads to a ularly favorable effect.

n our case, however, it is apparently the monova- i^+ cation which compensates the excess Gd^{3+} charge. s confirmed by the case in which $SrCl_2$ is used as x, so that the compensating monovalent cation is t. As seen in Figs. 1 and 2 and Table 2, the flux ning chlorine not only does not increase the con- tion of Gd penetrating into the lattice, but on the ry has a negative effect. This may be explained remember that the chlorine also becomes included lattice.

röger et al.[3-5] have shown in the case of ZnS that tually replaces S^{2-} in the host lattice, thus reduc- negative charge at the anion lattice sites. In words, this effect is equivalent to the presence in tice of an uncompensated positive charge. How- on penetrating into the lattice, Gd^{3+} itself intro- an excess positive charge, which must be some- mpensated. Since the amount of chlorine intro- constitutes, say, 15% of the weight of strontium, the amount of gadolinium is only 0.01%, the effect chlorine in this case is overwhelming.

milarly, we could assume that in the phosphor with F flux, fluorine also has a negative effect like that rine, even though it has been shown[6-8] that F is ffective than Cl, Br, or I. Nevertheless, in order dy the effect of fluorine, we prepared the d(10^{-4})(Li_2CO_3) phosphor which contains only one valent cation—Li. As shown in Figs. 2 and 3 and 2, the concentration of the gadolinium activator ed in the SrS lattice under the action of this flux is greater than in the case of the phosphor with the ux.

o satisfy ourselves once more that the inclusion of alent activator into a divalent host lattice requires ovalent cation to compensate for the excess charge, ed Na_2CO_3 as the flux. As shown in Fig. 3, this flux ncreases the concentration of the gadolinium acti- vator, although to a smaller extent than Li_2CO_3. This may possibly be connected with the difference in the cationic radii of Li^+ and Na^+.

These last experiments make it possible to explain the unusually small amount of light stored in the SrS:Eu,Sm($SrCl_2$) phosphor.

As was shown in ref. 9, Sm^{3+} plays a large part in the storing of light by the phosphor, since it creates deep electron traps. In the SrS:Eu,Sm phosphor with the $SrCl_2$ flux, the trivalent samarium Sm^{3+} (as well as the trivalent gadolinium Gd^{3+} in the SrS:Eu,Gd phosphor) probably also penetrates the lattice poorly. As a result, the deep levels on which electrons can be localized are absent. This leads to a small light sum storage in this phosphor as compared to SrS:Eu,Sm (without flux), and particularly as compared to the SrS:Eu,Sm(LiF) phosphor.

We note, in conclusion, that since all rare earths (except Eu^{2+}) enter into the divalent SrS lattice in a trivalent state we may formulate the following rule: In preparing a phosphor with SrS as host and rare earth activators, in order to insure better penetration of the activators into the host lattice, we must choose a flux which contains a monovalent cation which plays an essential part in compensating for the excess charge in the lattice.

I wish to express my appreciation to V. V. Antonov-Romanovskii, who directed this work, to M. V. Fok for his constant interest in it, and to R. M. Medvedeva for the preparation of the phosphors.

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STUDY OF ELECTRICAL CONDUCTIVITY AND OPTICAL TRANSMISSION OF THIN LAYERS OF CERTAIN INTERMETALLIC COMPOUNDS OF ANTIMONY

Yu. G. Belashov and L. V. Belashova (pp. 523-526)

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This paper is devoted to a study of some optical and electrical properties of the intermetallic compounds CdSb, Mg_3Sb_2, and InSb. The dependence of conductivity on concentration of the components in the binary systems and also the spectral dependence of the transmission of these systems were investigated; consideration was also given to the possibility of using these materials as optical media.

EXPERIMENTAL METHOD

The experiments were conducted in a vacuum chamber which could maintain a vacuum of the order of 2×10^{-5} mm Hg during the evaporation process. The materials were evaporated from tungsten boats. The substrates consisted of materials which were transparent in appropriate parts of the spectrum. In the case of CdSb and Mg_3Sb_2, type K-8 glass and thin platelets of mica were used, while plates of synthetic CaF_2 were used for InSb.

Layers with various concentrations of the components were obtained by two methods. The first method, which was used in the experiments with CdSb and Mg_3Sb_2, has been described by Vekshinskii[1] and consists of the simultaneous vaporization of the components from two different evaporators in such a way that the required concentrations of the materials were deposited onto the substrate. The disposition of the evaporators and the samples was chosen in such a way that a stoichiometric layer was obtained on the central sample and the samples at the edges had a ratio of components equal to 1:5 after completion of the evaporation. Calculated values of the layer thicknesses agreed within 5% with results of measurements made by means of an MII-4 microinterferometer.

The evaporation conditions were chosen so that the sublimation of the various components effectively occurred within the same time periods. The evaporators were cut on at the beginning and cut off at the end of a period with the help of a special shielding apparatus.

The second method, which was used in the experiments with InSb, consisted of evaporation of an InSb layer from a polycrystalline melt. The indium antimonide preparation was made by melting the components, which were combined in amounts proportional to their atomic weights, in a thick-walled pyrex ampoule; the ampoule containing the starting materials was preheated to a temperature of 350°C under a vacuum of about 5×10^{-6} mm Hg and was then sealed off. The ampoule was maintained at 550°C for about 5 hr in order to homogenize the material; afterwards it was cooled slowly to a temperature of 200°C (at a rate of 3 to 5 deg/min) and it was then removed from the furnace.

All the starting materials were spectroscopically pure with the exception of the cadmium, which was obtained by mechanical cleaning of a granule of grade-ChDA cadmium. Both the samples and the evaporators were carefully degassed before sublimation and the substrate was cleaned by electron bombardment for 5 to 7 min.

EXPERIMENTAL RESULTS

Cadmium Antimonide. Figure 1 shows a plot of electrical conductivity σ of a CdSb layer as a functi the weight concentration of the components. The mi mum in the curve, corresponding to a layer which i actly stoichiometric, has a value of 3×10^{-2} ohm^{-1} Note that in the experiments performed by Mochan a study of ZnSb layers produced by evaporation in a vacuum, a similar dependence was reported. Clearl conclusions reached in that paper concerning the na and character of this dependence can be carried ove the Cd-Sb system.

Samples with the smallest conductivity were as rule characterized by the highest transmission in th ible and near infrared; the transmission increased siderably with wavelength. The samples with lowest conductivity had brownish-red color by transmitted

In order to decrease the reflection coefficient stoichiometric layer of CdSb whose geometric thick was about 300 mμ, this layer was covered by a laye magnesium fluoride. This treatment led to a marke crease in transmission in the 4.5 μ region. Then an layer of CdSb of the same thickness as the first one deposited by sublimation. As one ought to have expe this procedure caused a change in the shape of the s tral dependence of the transmission and a shift of th maximum toward lower wavelengths. The results o spectral measurements made with the help of an IK spectrophotometer are shown in Fig. 2.

Magnesium Antimonide. The study of the depen of the electrical conductivity of Mg-Sb layers on the centrations of the two constituents led in general to

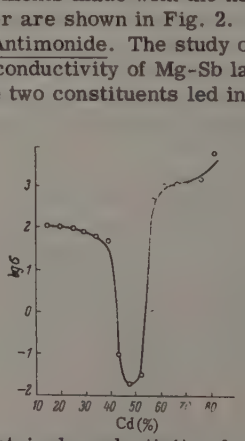

Fig. 1. Electrical conductivity of a CdSb layer as a function of the weight concentrations of components.

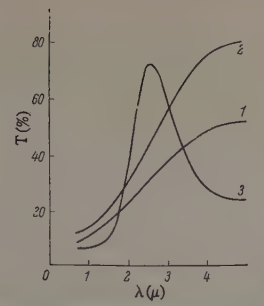

Fig. 2. Spectral dependence of the transmission coefficient of a CdSb layer. Curve 1—untreated layer; curve 2—layer made transparent in the 4.5 to 5 μ region by magnesium fluoride; curve 3—three-layer system.

similar to those described above for the Cd-Sb s. In the range of concentrations corresponding to rmula Mg_3Sb_2, a substantial decrease (by 2 or 3 s of magnitude) in electrical conductivity was ob- d, but lack of reproducibility in the results made it ssible to decide on the value at the minimum. The um in electrical conductivity was also associated maximum in transmission in the visible and near ed. This is illustrated in Fig. 3a, which shows the mission curves. The change in transmissivity of yer with position along the sample was exactly the as that described by Kurov,[3] namely, that the trans- on was high for samples of stoichiometric composi- nd that there was a sharp transition to opacity on agnesium-rich side and a gradual transition on the ony-rich side. The thickness of the layer mea- with an MII-4 microinterferometer amounted to μ.

rom the transmission spectra shown in Fig. 3a, it ar that thin layers of Mg_3Sb_2 constitute a material is very transparent in the infrared.. The trans- vity in the visible part of the spectrum decreases ecreasing wavelength. The layer becomes prac- opaque to light of wavelength shorter than 0.5 μ. amples with excess magnesium have a much lower missivity because a large fraction of the light is ted. These samples have a luster approaching f a magnesium mirror. The samples with excess ony, which appear dark by reflected light, are more arent. Thus the behavior of the transmissivity re- similar to that described by Kurov[3] even outside sible region.

lowever, we did not consider it necessary to as- te the transmissivity with formation of oxides and tes and disturbances of the basic crystal structure compound. A more probable process is that the al structure becomes ordered as the stable phase med, which in the light of band theory and the op- f semiconductors can easily lead to a decrease of ical conductivity and an increase in transmissivity. alidity of such an approach can be substantiated by uring the photoconductivity and establishing the ex- e of a very narrow forbidden energy gap in the en- spectrum of the Mg_3Sb_2 lattice; this topic has been ed in detail in the paper by Zhuze et al.[4]

n order to decrease the reflection coefficient, a s of samples with varying concentrations of com- ts in the layer were covered by magnesium fluo- ilms with optical thickness of 0.6 μ at λ = 2.4 μ.

The transmission coefficient of samples of stoichiometric composition reached 93%. This fact indicates that the material has a very small absorption coefficient in this part of the spectrum.

Light filters prepared from Mg-Sb layers made transparent by means of the indicated process have transmission spectra like those shown in Fig. 3b. The low contrast of such light filters is evidently caused by the small value of the reflection coefficient of the Mg-Sb layers.

Indium Antimonide. Present day interference filters of the Fabry-Perot type which are intended for use in the infrared (beyond 2 μ) usually utilize multiple-layer dielectric interference reflectors, which although they have an advantage in light transmission, lead to considerable difficulty in the preparation of optical filters (the necessity of strict control of the thickness of each layer, the long time required for the experiment, the rather considerable total thickness of the multiple layer system, etc.).

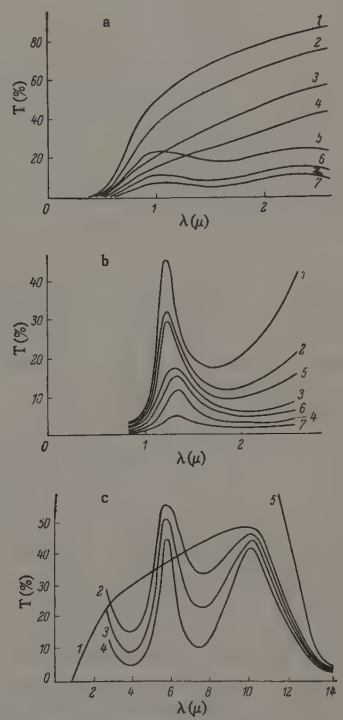

Fig. 3. Spectral dependence of the transmission coefficients of single layers and multiple layer filters of Mg-Sb (a,b) and InSb (c). a—single layer: curve 1—layer of stoichiometric composition; curves 2-4—layers with increasing amounts of excess antimony; curves 5-7—layers with increasing amounts of excess magnesium. b—three-layer filter: curve 1—reflecting stoichiometric layer of Mg_3Sb_2; curves 2-4—layer of Mg_3Sb_2 with increasing amounts of excess antimony; curves 5-7—layers of Mg_3Sb_2 with increasing amounts of excess magnesium. c: curve 1—single layer 120 mμ thick; curves 2-4—single, double, and triple layers, respectively, with half-wave interlayers of MgF_2; curve 5—substrate of CaF_2.

At the outset of the experiments with indium antimonide, we started with the following information; firstly, as was shown by Welker and Weiss,[5] the index of refraction of InSb is equal to 4.1, which ensures a high reflection coefficient; secondly, according to the data of Welker,[6] Cunnell and his co-workers,[7] and a number of other authors,[8,9] this compound has a very small absorption coefficient in the infrared; and finally, the presence of absorption bands in InSb in the visible and near infrared regions of the spectrum should lead to a considerable decrease in the background for these parts of the spectrum.

In order to test this assumption, the spectral dependence of the transmission coefficients of single layers of InSb and of single, double, and triple layer light filters based on this material plus half-wave interlayers of magnesium fluoride was studied. The single layers of InSb prepared by sublimation from a polycrystal had the same sort of transmission characteristic as that obtained by Konozenko and Mikhnovskii.[10] Figure 3c shows a transmission curve for a single layer of InSb, 120 mμ thick. It should be noted that the rate of deposition was considerably higher in our case than in the reference cited (at a distance of 350 mm from the surface of the evaporator a layer of about 20 mμ thickness was deposited in 1 min). It was noted that layers prepared at slower evaporation rates had a higher optical absorption.

In the composite systems the thickness of the InSb layers was again set equal to 120 mμ. Their optical thicknesses nd, under the assumption that the index of refraction in the layers was the same as in bulk samples, was equal to 490 mμ. This amounts to about 0.1 λ_{max}, where λ_{max} is the wavelength at the transmission maximum. Therefore, to a reasonably good approximation one could assume that the interference of light in the InSb layer had no essential effect on the transmission of the optical filters. In the case considered here, the geometrical thickness of the MgF_2 was 2μ. Figure 3c shows three curves which give an idea of the change in contrast associated with an increase in the number of layers in the interferometer. The decrease of transmission in the region beyond 10 μ (Fig. 3c) is caused by adsorption in the substrate. This is illustrated by the transmission curve of a pure calcium fluoride substrate.

Because of the fact that the contrast of the filters described above was unsatisfactory, which probably resulted from the fact that the reflection coefficient of the InSb layer was not high enough, an attempt was made to prepare an optical filter from indium antimonide doped with indium in a ratio of about 1:50. As is evident from Fig. 4, the use of the doped material led to a decrease in the background and to an increase of contrast in the filter. This effect can be explained by an increase in the reflection coefficient of the InSb layer unaccompanied by any significant increase of absorption in it.

Thus thin layers of magnesium antimonide and indium antimonide constitute materials which are highly

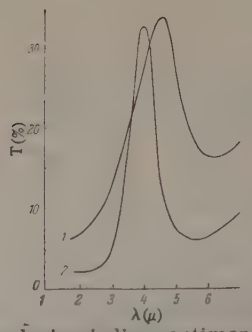

Fig. 4. How doping indium antimonide with indium affects the parameters of a single layer filter. Curve 1—interferometer with undoped InSb reflectors; curve 2—interferometer with reflectors of InSb doped with 2% excess indium.

transparent in the infrared and one can prepare wide-band infrared absorption type optical filters from the The authors did not succeed in obtaining good narrow-band Fabry-Perot type interference filters made fro InSb, but the possibility of obtaining a considerable i provement in the parameters of such filters by using doped material has not been eliminated.

The authors express their indebtedness to V. F. Suetin for reading the manuscript and for a number o important comments.

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DETERMINATION OF THE MICROCHARACTERISTICS OF SILVER AND GOLD FROM THE INFRARED OPTICAL CONSTANTS AND THE CONDUCTIVITY AT 82 AND 295°K

V. G. Padalka and I. N. Shklyarevskii (pp. 527-535)

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Measurements were made of the optical constants of silver and gold in the wavelength range 1-12 μ and of the electrical conductivity of the same specimens at 82 and 295°K. The values obtained were used to determine the microcharacteristics of these metals—the electron concentration in the conduction band, the velocity at the boundary of the Fermi surface and the electron-electron, electron-phonon, and electron-impurity collision frequencies. Comparisons were made with the results of electronic specific heat and radio-frequency surface impedance measurements.

ODUCTION

n certain metals, several parameters of importance physics of metals can be determined from a study infrared optical properties, combined with con-ity measurements; these parameters are the free on concentration N, the Fermi velocity v, the elec-electron collision frequency ν_0^{ee}, the electron-pho-llision frequency ν_0^{ef}, and the electron-impurity or on-lattice defect collision frequency ν^{ed}.

For certain high-conductivity metals (Ag, Au, Cu) notoconductivity edge lies in the visible or near in-d, so that the absorption of electromagnetic energy infrared is determined by electrons in the conduc-and. At room temperature, and even more so at mperatures, the skin effect will be anomalous. $l \sim \delta$ or $l \gg \delta$, where l is the electron free path is the skin depth, there is no local correlation be-current and field; Ohm's law in its classical formu-does not apply and the current at a given point in etal is determined not by the field only at that point so by the field in a certain surrounding region. the experimentally determined refractive index μ e absorption index $\mu\chi$ must be understood as ef-é values.

Dingle,[1] using a classical kinetic equation, obtained equency dependence of the complex dielectric con-$\tilde{\varepsilon} = (\mu - i\mu\chi)^2$ and the absorption coefficient A in frared for an anomalous skin effect. With isotropic rsion and diffusive electron scattering by the metal ce (which probably occurs[2,3]), and where the condi-

$$\frac{v}{\omega} \ll \delta; \qquad \nu_{eff.} \ll \omega \ll \omega_0, \tag{1}$$

atisfied, where $\nu_{eff.}$ is the effective collision fre-y, ω_0 is the photoconductivity edge, and ω is the ar frequency of the incident light, the real part of omplex dielectric constant $\mu^2 - (\mu\chi)^2$ and the ab-ion coefficient A depend on the wavelength of the ent light as follows:

$$\mathrm{Re}\,\tilde{\varepsilon} \equiv \mu^2 - (\mu\chi)^2 = -8.954 \cdot 10^{-22}(1 - p^2G)N\lambda^2, \tag{2}$$

$$M \equiv \frac{4\mu}{(\mu\chi)^2 + (\mu+1)^2} = \frac{3}{4}\beta + 3.546 \cdot 10^{-5}N^{-1/3}\nu_{eff.} - p^2qD. \tag{3}$$

Here $\beta = v/c$; $p^2 = 6.716 \times 10^{-22}\beta N\lambda^2$; $q = 2.047 \times \nu_{eff.}/\sqrt{N}\beta$; $G = 0.3136 + 1.082q + q^2$; $D = 0.2137 + 0.750q + 0.750q^2 + 0.216q^3$; where λ is in microns and the effective mass of the electron is assumed equal to the mass of the free electron, that is, $m^* = m$.

In ref. 1, $\nu_{eff.}$ is understood to be the effective static frequency. However, as is shown in refs. 4 and 5 the effective electron collision frequency when the metal is in an infrared electromagnetic field is considerably different from the static collision frequency.

The effective frequency $\nu_{eff.}$ is the sum of the frequencies of electron-electron collisions ν^{ee}, electron-phonon collisions ν^{ef}, and electron-impurity collisions ν^{ed}. That is,

$$\nu_{eff.} = \nu^{ee} + \nu^{ef} + \nu^{ed}. \tag{4}$$

According to Gurzhi's results,[4] the effective electron-electron collision frequency ν^{ee} is related to the classical frequency ν_0^{ee} by:

$$\nu^{ee} = \nu_0^{ee}\left[1 + \left(\frac{\hbar\omega}{2\pi kT}\right)^2\right]. \tag{5}$$

Since $\hbar\omega \gg kT$ in the infrared, the value of ν^{ee} considerably exceeds the classical electron-electron collision frequency.

From a consideration of the quantum kinetic equation, the effective electron-phonon collision frequency ν^{ef} in the infrared may be shown[5] to be related to the classical frequency by the equation:

$$\nu^{ef}(T) = \nu_0^{ef}(T)\, f\left(\frac{T}{\theta}\right), \tag{6}$$

where θ is the Debye temperature If $\hbar\omega \gg kT \gg k\theta$, then $f(T/\theta) \approx 1$ and $\nu^{ef}(T) \approx \nu_0^{ef}(T)$. However, at $T \lesssim \theta$, the value of ν^{ef} is considerably different from ν_0^{ef}. For $\hbar\omega \gg k\theta \gg kT$ the classical electron-phonon collision frequency $\nu_0^{ef}(T)$ approaches zero and $\nu^{ef}(T)$ approaches the limiting value $(2/5)\nu_0^{ef}(\theta)$ where $\nu_0^{ef}(\theta)$ is the classical high temperature frequency for $T = \theta$. The function $f(T/\theta)$ is calculated in ref. 6.

The electron-impurity collision frequency ν^{ed} is independent of both temperature and wavelength of the incident radiation.

Motulevich[7] has considered Dingle's dispersion equations for the real and imaginary parts of the surface impedance, taking account of quantum corrections to the effective frequency $\nu_{eff.}$. We have used a similar equation for the real part of the complex dielectric constant in the present work, instead of an equation for the real part of the surface impedance. Substituting Eqs. (4), (5), and (6) into Eqs. (2) and (3), we transform the latter into:

$$\mathrm{Re}\,\tilde{\varepsilon} \equiv \mu^2 - (\mu\chi)^2 = -8.954 \cdot 10^{-22}\,(1 - p^2G)\,N\lambda^2; \qquad (7)$$

$$A \equiv \frac{4\mu}{(\mu\chi)^2 + (\mu+1)^2} = \frac{3}{4}\,\beta + 3.546 \cdot 10^{-5}\left\{\nu_0^{ef}(T)\,f\left(\frac{T}{\theta}\right) + \nu_0^{ee} + \nu^{ed}\right\} \cdot$$

$$N^{-1/3} + 1.861 \cdot 10^{12}\,\frac{\nu_0^{ee}}{T^2\sqrt{N}\,\lambda^2} - p^2\beta D. \qquad (8)$$

In Eqs. (7) and (8), p^2G and $p^2\beta D$ are correction terms, and these equations are solved simultaneously by successive approximations. In the first approximation, $p^2G = 0$, $p^2\beta D = 0$, and the slope of the linear function $\mu^2 - (\mu\chi)^2$ with respect to λ^2 in Eq. (7) determines N. We use this value of N in Eq. (8) and from the slope of the linear function A with respect to λ^{-2} we find the classical electron-electron collision frequency ν_0^{ee}. To determine ν_0^{ef} and ν_0^{ed} the electrical conductivity σ must be measured for the specimen under study, and the conductivity σ_m of the bulk metal used, since:

$$\nu_0^{ef} + \nu_0^{ee} = \frac{Ne^2}{m\sigma_M}; \qquad \nu_0^{ef} + \nu_0^{ee} + \nu^{ed} = \frac{Ne^2}{m\sigma}. \qquad (9)$$

Then from the intercept on the ordinate axis of the function A when plotted against λ^{-2} the velocity v on the Fermi surface for a given ν_0^{ef}, ν_0^{ee}, ν^{ed}, and N may be found. Further, when the values of the correction terms p^2G and $p^2\beta D$ have been determined, the next approximation may be found.

RESULTS OF THE MEASUREMENTS OF THE OPTICAL CONSTANTS OF SILVER AND GOLD

We have investigated the optical constants of silver and gold in the wavelength range 1-12 μ at temperatures of 295 and 82°K. The specimens were prepared by vacuum evaporation of the metals (purity better than 99.99%) onto a glass base. Evaporation was carried out in a vacuum of ~10^{-5} mm Hg, obtained with an oil vapor diffusion pump and a liquid nitrogen trap to freeze out the oil vapor. The evaporators (two tantalum crucibles) were placed under the specimens in such a way that the metal film thickness was uniform to within 5-8% over the whole specimens.

Shklyarevskii and Miloslavskii's method[8] was used to measure the optical constants; the specimens were placed in a cryostat,[9] the reservoirs being filled with liquid nitrogen for the low temperature measurements. Since the light was incident on the cryostat window at angles close to normal (the maximum angle of incidence was 13°), polarization of the light by the cryostat window introduced a negligible error into the values of the optical constants.

Several pairs of specimens were measured, the results reproducing well. After the specimens were warmed from 82 to 295°K the optical constants had the same values as before the films were cooled.

Figure 1 shows the absorption coefficient $\mu\chi$ (curve 1, left-hand scale) and the refractive index (curve II, right-hand scale) for silver (a) and gold (b). The solid curves are for T = 295°K (open circles) and the dashed curves are for T = 82°K (dots). The results of the measurements on the optical constants of silver at room temperature in the 1-7 μ range agree well with our earlier results;[10] in the range of wavelengths greater than 7 μ the values of μ and $\mu\chi$ were lower than the earlier values. The lower accuracy (higher values) for the optical constants of silver in the long wavelength region[10]

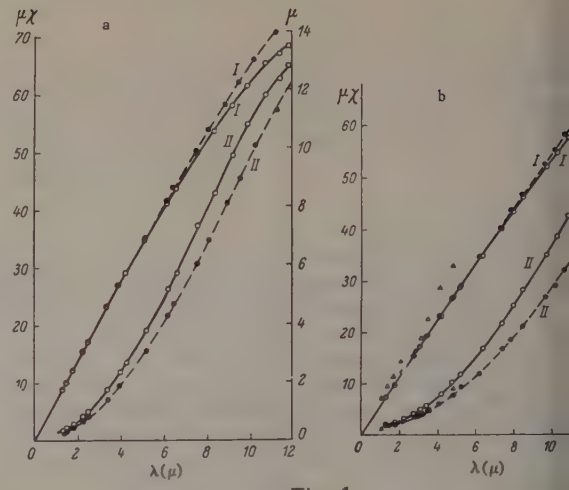

Fig. 1

results from experimental difficulties, as was shown ref. 11; we were able to overcome these in the preser work. Reference 10 gives a comparison of our values μ and $\mu\chi$ with those of other authors, for the region 1-6 μ.

The values obtained for the absorption coefficien $\mu\chi$ for gold at room temperature agree with the earli results[12] to within a few percent, for the whole wavele range 1-12 μ. However, the refractive index μ is con siderably lower than in the earlier work.[12] This show that the gold films used in the earlier work[12] were no sufficiently pure; in particular, the gold was evaporat from molybdenum, not tantalum, crucibles, which lea to contamination of the evaporated films, as shown in ref. 13. The triangles in Fig. 1b show the values obta by Försterling and Fredericksz[14] on electrochemicall deposited gold films.

To permit a more convenient comparison of the r sults for the temperatures 295 and 82°K, Tables 1 an give the refractive index μ and the absorption coeffic $\mu\chi$ for silver and gold respectively, for integral wave lengths, taken from the curves of Fig. 1. The absorpt coefficients $\mu\chi$ in the 1-6 μ range remain unaltered the temperature is reduced, while in the range 6-12 μ they increase slightly. The refractive indices μ fall considerably over the whole wavelength range investi gated.

RESULTS OF CONDUCTIVITY MEASUREMENTS

To determine the conductivity σ, it is necessary know the thicknesses of the films, and these were obt

Table 1

Silver

λ(μ)	T = 295° K		T = 82° K	
	μ	μχ	μ	μχ
1	0.25	6.81	0.22	6.81
2	0.68	13.6	0.57	13.6
3	1.38	20.3	1.14	20.3
4	2.34	26.9	1.92	26.9
5	3.52	33.2	2.88	33.5
6	4.87	39.4	4.02	39.9
7	6.31	45.3	5.31	46.1
8	7.86	50.9	6.70	52.1
9	9.36	56.0	8.10	57.8
10	10.8	60.7	9.60	63.5
11	12.0	64.8	10.9	68.3
12	12.8	67.8	—	—

Table 2

Gold

λ(μ)	T = 295° K		T = 82°
	μ	μχ	μ
1	0.31	5.58	0.28
2	0.54	11.2	0.45
3	0.93	16.7	0.74
4	1.49	22.2	1.15
5	2.19	27.7	1.67
6	3.01	33.0	2.29
7	3.97	38.3	2.99
8	5.05	43.5	3.84
9	6.21	48.6	4.74
10	7.41	53.4	5.70
11	8.71	58.2	6.76

ing lines of equal chromatic order;[15] the values lay range 0.7-1.1 μ. The silver specimens had a conity $\sigma = 3.1 \times 10^{17}$ cgs units at T = 295°K and $\sigma =$ 10^{17} cgs units at T = 82°K. According to ref. 16 onductivity of bulk silver is $\sigma_m = 5.6 \times 10^{17}$ cgs at T = 295°K and $\sigma_m = 2.9 \times 10^{18}$ cgs units at T =

At room temperature the conductivity of the gold studied was $\sigma = 2.65 \times 10^{17}$ cgs units (according to 6 bulk gold has $\sigma_m = 4.06 \times 10^{17}$ cgs units). At $\sigma = 5.6 \times 10^{17}$ cgs units (according to ref. 16 bulk at T = 82°K has $\sigma_m = 1.9 \times 10^{18}$ cgs units).

JSSION OF THE RESULTS

By successive approximations, Eq . (7) and (8) were d simultaneously, using the measured optical con- s for the wavelength range 1-12 μ and the measured ical conductivity of the samples. Figure 2 shows nction

$$\frac{\mu^2 - (\mu\chi)^2}{1 - p^2G} = f(\lambda^2)$$

.) silver and (b) gold. The experimental results lie to the straight lines through the origin, both for temperature (open circles) and for the low temper- (dots). The slopes of these straight lines give the electron concentrations.

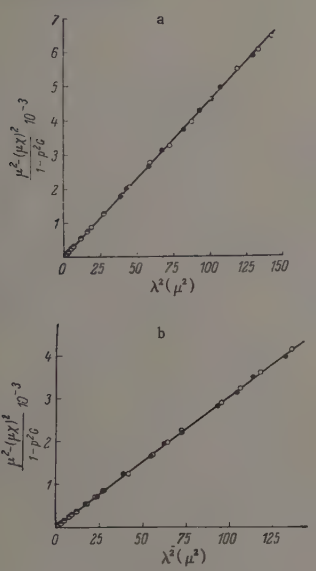

Fig. 2

Figure 3 shows the relationship $A + p^2\beta D = \varphi(\lambda^{-2})$.) silver and (b) gold. Again, the experimental re- for room temperature (open circles) and the low erature (dots) lie close to the straight lines, the s of which give ν_0^{ee}. Table 3 gives the microcharac- tics of silver and gold films determined from the ght lines of Figs. 2 and 3.

By weighing the specimens on microbalances we es- shed that the filling factor of the films was close to . with values 0.97-0.99. Therefore the atomic con- ation in the bulk specimens of the metals can be for the concentrations in the silver and gold films.

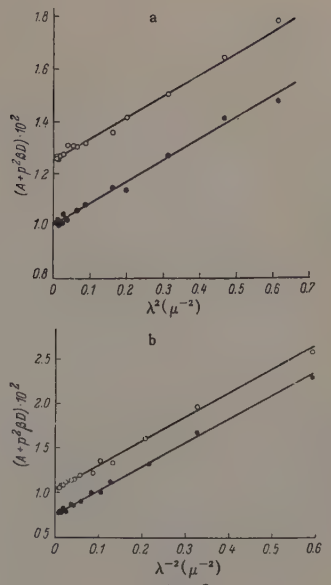

Fig. 3

As is to be expected, the electron concentration in the conduction band remains unaltered as the temperature is reduced from 295 to 82°K for both metals, owing to the considerable energy gap between the valence and the filled bands. The Fermi velocity v does not alter either, since the limiting Fermi energy $\varepsilon_0 \gg kT$.

At room temperature the function $f(T/\theta)$ is equal to 1.03 for silver and 1.00 for gold (according to ref. 17 the Debye temperature is 215°K for silver and 180°K for gold). Thus the electron-phonon collision frequency ν^{ef} in the infrared practically coincides with the classical value ν_0^{ef} for these metals. When the temperature is reduced to 82°K the electron-phonon collision frequency ν_0^{ef} decreases considerably. Since the low temperature measurements were made at a temperature far below the Debye temperature, $\nu^{ef} = 0.52\nu_0^{ef}(\theta)$ for silver and $0.57\nu_0^{ef}(\theta)$ for gold, close to the limiting value $\nu^{ef} = 0.4\nu_0^{ef}(\theta)$. Thus further reduction in temperature does not appreciably alter the electron-phonon collision frequency relative to that determined at 82°K.

Figure 3 shows the parallel straight lines through the experimental points for temperature 295°K (open circles) and 82°K (dots). Since the slope of the straight lines is given by the ratio ν_0^{ee}/T^2, the value of ν_0^{ee} is proportional to T^2, which agrees with the theoretical relationship. Our values are somewhat higher than the classical values of the electron-electron collision frequency ν_0^{ee} obtained for silver and gold by Lameris[1] from calorimetric measurements of the absorption coefficients.

The dimensions of the silver and gold crystals formed by thermal evaporation can be estimated from the electron-lattice defect collision frequency ν^{ed} (as-

Table 3

Metal	T(°K)	$N_a \times 10^{-22}$ (cm^{-3})	$N \times 10^{-22}$ (cm^{-3})	$\nu_0^{ee} \times 10^{-13}$ (sec^{-1})	$\nu_0^{ef} \times 10^{-13}$ (sec^{-1})	$\nu^{ef} \times 10^{-13}$ (sec^{-1})	$\nu^{ed} \times 10^{-13}$ (sec^{-1})	$v \times 10^{-8}$ (cm/sec)
Ag	295	5.9	5.2	9.2	2.26	2.33	1.9	2.3
	82	5.9	5.2	0.7	0.45	0.87	1.9	2.3
Au	295	5.9	3.5	24.2	1.94	1.94	1.1	1.6
	82	5.9	3.5	1.85	0.45	0.74	1.1	1.6

suming that the grain boundaries are the only defects). This gives $D \approx v/\nu^{ed} \approx 1000$ A for silver and ≈ 1500 A for gold.

Since the effective electron-electron collision frequency ν^{ee} varies with the wavelength of the incident light, the quantity $\nu_{eff.} = \nu^{ee} + \nu^{ef} + \nu^{ed}$ and the free path $l = v/\nu_{eff.}$ will also vary with frequency. For a wavelength of 6 μ, we have, for silver:

at T = 295°K, $\nu_{eff.} \approx 4.5 \times 10^{13}$ sec^{-1}, $l \approx 5 \times 10^{-6}$ cm;
at T = 82°K, $\nu_{eff.} \approx 2.9 \times 10^{13}$ sec^{-1}, $l \approx 8 \times 10^{-6}$ cm.

Similar values for the same wavelength for gold are:

at T = 295°K, $\nu_{eff.} \approx 3.8 \times 10^{13}$ sec^{-1}, $l \approx 4 \times 10^{-6}$ cm;
at T = 82°K, $\nu_{eff.} \approx 2.3 \times 10^{13}$ sec^{-1}, $l \approx 7 \times 10^{-6}$ cm.

The skin depth δ varies little with temperature and wavelength and is given by $\delta = \lambda/2\pi\mu\chi \approx 2.4 \times 10^{-6}$ and $\approx 2.9 \times 10^{-6}$ cm for silver and gold respectively. Therefore at the temperatures used $l \sim \delta$ in this wavelength range and a slightly anomalous skin effect occurs.

Equations (7) and (8), which we used, are valid under the following conditions:

$$\frac{v}{\omega\delta} \ll 1; \qquad \frac{\nu_{эфф.}}{\omega} \ll 1; \qquad \omega_0 \gg \omega.$$

The first two of these inequalities can be directly verified. For silver at $\lambda = 6\ \mu$, the quantity $v/\omega\delta = 0.3 \ll 1$; at $\lambda = 6\ \mu$ we have $\nu_{eff.}/\omega = 0.14 \ll 1$ at T = 295°K and $\nu_{eff.}/\omega = 0.09 \ll 1$ at T = 82°K. For gold at $\lambda = 6\ \mu$ $v/\omega\delta = 0.17 \ll 1$; for the same wavelength $\nu_{eff.}/\omega$ is 0.12 and 0.07 for room temperature and the low temperature, respectively. The criterion for satisfaction of the third inequality is the linearity of the function $A + p^2\beta D$ with respect to λ^{-2} and the independence of N, determined by Eq. (7), with respect to wavelength. The straight lines for (a) silver and (b) gold in Figs. 3 and 4 confirm that $\omega \ll \omega_0$.

It is of some interest to compare the microcharacteristics that we obtained with the results of radio-frequency surface impedance and electronic specific heat measurements on silver and gold.[18] From radio-frequency surface impedance measurements we can determine the quantity:

$$\frac{v}{N} = \frac{e^2}{m\left(\frac{\sigma_0}{l}\right)} = \frac{2.53 \cdot 10^8}{\frac{\sigma_0}{l}}. \qquad (10)$$

Surface impedance measurements for silver[19] give, according to Eq. (10), $v/N = 3.1 \times 10^{-15}$ cm^4 sec^{-1}. From our measurements, $v/N = 4.4 \times 10^{-15}$ cm^4 sec^{-1}. For gold, surface impedance measurements[19] give $v/N = 3.3 \times 10^{-15}$ cm^4 sec^{-1}. Our measurements give $v/N = 4.6 \times 10^{-15}$ cm^4 sec^{-1}.

Measurements of the electronic specific heat γ enable us to determine the quantity:

$$\frac{v}{\sqrt{N}} = \frac{\pi k}{\sqrt{m\gamma}} = \frac{1.44 \cdot 10^{-2}}{\sqrt{\gamma}}, \qquad (11)$$

where k is Boltzmann's constant and $C^{(e)} = \gamma T$ is the electronic contribution to the specific heat of the metal. According to ref. 20, Eq. (11) gives for silver: $v/\sqrt{N} =$

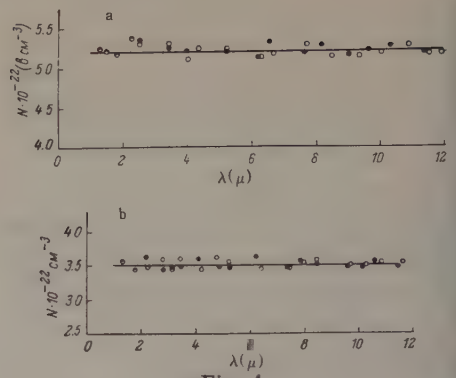

Fig. 4

0.56×10^{-3} cm$^{5/2}$ sec^{-1}. According to our measureme $v/\sqrt{N} = 1 \times 10^{-3}$ cm$^{5/2}$ sec^{-1}. For gold,[18] $v/\sqrt{N} = 0.56$ cm$^{5/2}$ sec^{-1}. From our measurements; $v/\sqrt{N} = 0.85 \times$ cm$^{5/2}$ sec^{-1}.

Of course, these comparisons are only semiquan tive, since the measurements of the electronic specif heat and the surface impedance were made on differe specimens from those used in our experiments.

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OPTICAL CONSTANTS OF CADMIUM OXIDE IN THE INFRARED

V. K. Miloslavskii and A. I. Ranyuk (pp. 536-541)

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Optical constants of the semiconductor CdO were measured in the wavelength interval 1.5-7 μ for different carrier concentrations. It was shown that absorption in this region is a function of electron conduction. The effective mass and mobility of the electrons for concentrations of 10^{20} to 10^{21} cm^{-3} were calculated using the classical theory of high frequency conduction. The dependence of mobility on the excess cadmium ion concentration was found by the optical method and is explained by the theory of Conwell and Weisskopf.

ODUCTION

Cadmium oxide is a semiconductor with a high con- ration of carriers and has properties similar to those etals. The high conductivity of CdO is due to the ence of a large concentration of excess cadmium m arises from the usual manner of preparation (sin- g or cathode sputtering) as a result of partial dis- tion of the oxide.

The electrical properties of CdO have been rather studied.[1-4] However, investigation of the electrical erties alone does not make possible adequate de- ination of such an important characteristic of car- behavior in a semiconductor as effective mass.[5] ew papers[6,7] devoted to the optical properties of have shown that absorption in the infrared region arge electrical conductivity depends on the car- and increases as the electron concentration grows. It is well known that the effective mass of carriers be found by determining the optical constants of conductors in the infrared region while at the same measuring the Hall constant of the same sample.[8] method is at present essentially the only one for conductors with high impurity concentration and l carrier relaxation times. Thus the optical method nding effective masses is very convenient for de- rate semiconductors and semiconductors which have prepared as polycrystalline samples.

CRIPTION OF THE EXPERIMENT AND RESULTS OF THE MEASUREMENTS

The cadmium oxide samples were prepared as thin rs (0.2 to 1 μ thick) by cathode sputtering. Such rs have reflecting surfaces and are of uniform thick- over a broad area (4×4 cm^2). By changing the con- ns of cathode sputtering one can obtain layers with rent concentrations of excess cadmium and thus with rent electrical and optical properties.[6,9] Moreover lectrical properties change as a result of prolonged treatment in different gases.[4,9] By using different ods of preparation we obtained samples with elec- concentrations from 1.32×10^{20} to 12.1×10^{20} cm^{-3}. To find the optical constants of CdO in the infrared on we used the method of Avery.[10] The essence of method is to determine the ratio r_p/r_s (r_p and r_s the coefficients of reflection for light polarized in perpendicular to the incident plane) for three angles cidence and then to calculate the optical constants hically.

In the case of our large carrier concentrations the polarization method appeared more convenient because the samples become opaque for wavelengths $\lambda > 2\ \mu$, which greatly limits the possibilities of methods which measure transmission. The apparatus used to measure the polarized light intensities was set up at the input of an IKS-6 spectrometer. A system of four pairs of parallel mirrors M_1, M_2, M_3, and M_4 (Fig. 1) was used to determine the intensities of reflected light for different angles of incidence onto the sample while the source O was kept fixed relative to the slit S. The sample under investigation (mirror M_1) was placed at the axis of a goniometer provided with a vernier dial. As a polarizer we used the usual selenium stack with an entrance aperture 3 centimeters square. To better illuminate the slit the image of the source was focused onto it by means of the focusing apparatus F_1 and F_2. Analysis shows that use of narrow diverging beams (a divergence angle of 5°) instead of parallel rays introduces no substantial systematic error into the determination of the ratio r_p/r_s.

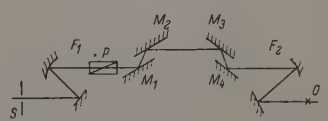

Fig. 1

To eliminate errors from the polarization of light by the apparatus and by the measuring instrument we first determined the intensity ratio I_p/I_s for light reflected from a sample with known optical constants (silver[11]).

Figure 2 (a and b) presents the results of typical measurements of the optical constants of two CdO samples with different carrier concentrations. From the graphs it is evident that the spectra of the optical constants are analogous to those of metals; there is a region of high reflectivity ($k > n$) and a region transparent to short wavelengths ($n \gg k$). The wavelength λ_0 for which k equals n is located in the near infrared and moves toward the short wavelength region as the car-

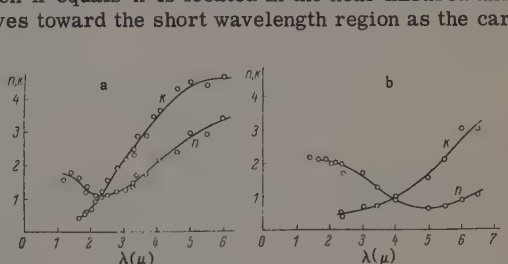

Fig. 2. a—N = 12.1×10^{20} cm^{-3}; b—N = 1.32×10^{20} cm^{-3}.

rier concentration increases (for $N = 1.32 \times 10^{20}$ cm^{-3}, $\lambda_0 = 4.0$ μ; for $N = 12.1 \times 10^{20}$ cm^{-3}, $\lambda_0 = 2.25$ μ).

For most metals the corresponding wavelength is located in the ultraviolet region (cf. F. Seitz[12]). The accuracy of the determination of the optical constants varies for different spectral regions. The accuracy diminishes as the wavelength increases, because the intensity of the source (plug-in of IKR-1) decreases. In the transparent region $n \gg k$ the Avery method is not applicable and the index of refraction is determined from Brewster's angle. In the most favorable case (λ = 2 to 5 μ) the error is of the order of 10%.

BASIC RELATIONSHIPS IN THE THEORY OF HIGH FREQUENCY CONDUCTION OF SEMICONDUCTORS IN THE INFRARED

The solution to the Boltzmann equation describing the influence of a high frequency electromagnetic field on an electron gas leads to the following expression for the current density[13]:

$$j_x = \frac{-2e^2}{(2\pi)^3} \int V_x f_1 d\Omega_k = \sigma E_x + \alpha \frac{\partial E_x}{\partial t}. \quad (1)$$

Here the equilibrium distribution function is adjusted by a function f_1, the form of which is determined by the presence of a periodic electromagnetic field with electric vector $E_x = E_{ox} e^{i\omega t}$ directed along the x axis. $d\Omega_k = dk_x dk_y dk_z$ is the volume element in wave vector space (the integration is over all k-space).

The current density is broken into two parts—the conduction current σE_x and the displacement current $\alpha \partial E_x / \partial_t$.

The conductivity

$$\sigma = -\frac{2e^2}{(2\pi)^3} \int \frac{V_x \tau}{1 + \omega^2 \tau^2} \frac{\partial f_0}{\partial p_x} d\Omega_k \quad (2)$$

is expressed in terms of the equilibrium distribution function f_0 and the relaxation time τ. The polarization α has an analogous form

$$\alpha = \frac{2e^2}{(2\pi)^3} \int \frac{V_x \tau^2}{1 + \omega^2 \tau^2} \frac{\partial f_0}{\partial p_x} d\Omega_k. \quad (3)$$

Similar relations apply for the case of the normal skin effect when the depth of penetration of the electromagnetic field into the semiconductor is significantly larger than the electron mean free path. Most semiconductors completely satisfy this condition. Of particular interest is the frequency region where

$$\omega_i \gg \omega \gg \nu. \quad (4)$$

Here ω_i is the "red" limit of self absorption. For semiconductors with very wide forbidden bands (CdO, ZnO, and others) inequality (4) holds in the near infrared. In this case the polarization α is independent of the collision frequency $\nu = 1/\tau$

$$\alpha = \frac{2e^2}{(2\pi)^3 \omega^2} \int V_x \frac{\partial f_0}{\partial p_x} d\Omega_k = -\frac{2e^2}{(2\pi)^3 \hbar^2 \omega^2} \int \frac{\partial^2 E}{\partial k_x^2} f_0 d\Omega_k \quad (5)$$

(E is the electron energy).

If the quadratic law of dispersion $E = \hbar^2 k^2 / 2m^*$ is satisfied then Eq. (5) reduces to

$$\alpha = -\frac{Ne^2}{m^* \omega^2}. \quad (6)$$

and a measurement of the polarization is sufficient to find the effective mass m^*.

For strong degeneracy, the case which interests u the quadratic law of dispersion does not hold, because the effective mass is a function of the wave number. F any isotropic law of dispersion $E = E(k)$ Eqs. (2) and (3) become

$$\alpha = -\frac{Ne^2}{m' \omega^2}, \quad (7a)$$

$$\sigma = \frac{Ne^2 \nu_f}{m' \omega^2}, \quad (7b)$$

where the quantity

$$m' = \frac{\hbar^2 k_f}{\left.\frac{\partial E}{\partial k}\right|_{k=k_f}} = \frac{\hbar k_f}{V_f}$$

is the average effective mass over the conduction band V_F is the average velocity at the Fermi surface; and ν is the average collision frequency at the Fermi surfac and depends only on temperature and the frequency of incident light.

Thus by simultaneously determining the optical co stants n and k and the electron concentration N (Hall effect) it is possible to find the microcharacteristics and ν_F of electrons in semiconductors, since the real and imaginary parts of the dielectric constant equal

$$n^2 - k^2 = \varepsilon_0 + 4\pi\alpha, \quad (7a)$$

$$2nk = \frac{4\pi\sigma}{\omega} \quad (7b)$$

(ε_0 is the optical dielectric constant).

INTERPRETATION OF RESULTS

It follows from Eqs. (7a) and (7b) that in the short wavelength part of the spectrum the real part of the di electric constant $\varepsilon = n^2 - k^2$ should depend linearly on λ^2 (Fig. 3). The slope of the straight lines increases in proportion to the electron concentration. Samples with large concentrations exhibit deviation from a linear de pendence, the deviation being connected with the fact t condition (4) is no longer satisfied. The straight lines intersect the ordinate axis at the same point ($\varepsilon_0 = 5.6$ for samples with small concentration). It should be no that ε_0 decreases somewhat (to 4.8) as the concentrati of excess cadmium increases in the sample.

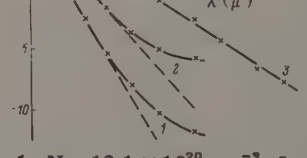

Fig. 3. 1—$N = 12.1 \times 10^{20}$ cm^{-3}; 2—$N = 6.55 \times 10^{20}$ cm^{-3}; 3—$N = 1.32 \times 10^{20}$ cm^{-3}.

The observed dependence of m' on the electron c centration is shown in Fig. 4. The magnitude of m' g from 0.39 m_e up to 1.19 m_e as the concentration increases from 1.32×10^{20} to 12.1×10^{20} cm^{-3}. The increase of the average effective mass is evidently rela to the complicated dependence of electron energy on

number.* The general theory of the motion of elec-

increase of m′ might also arise because the CdO e constant increases as a result of an increase of ss Cd.[16]

s in a periodic field reveals (cf. Dunlap[14]) a consid- le increase in effective mass with rise in the energy ectrons at the Fermi level. The position of the ni level in the conduction band depends on the elec- concentration, ultimately determining the depen- e of the average effective mass on concentration. value of the effective mass at the bottom of the con- on band is found by extrapolating the graph of m′ ro concentration and is 0.2 m_e, a value higher than .14 m_e found[7] in samples with carrier concentrations than 10^{20} cm^{-3}.

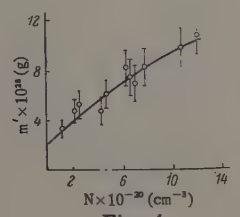

Fig. 4

The collision frequency ν_F can be found from the inary part of the dielectric constant [(8b) and (7b)]. neral the collision frequency depends on the wave- h. At the same time it is possible to convince one- Fig. 5) that the slope of the linear portion of the th of log 2nk against log λ has an average value of 3, rming the weak frequency dependence of ν_F. Thus, as to have been expected, the collision frequency s with increase in electron concentration (from 1.1 5 × 10^{14} sec^{-1} in the range of concentrations in- gated).

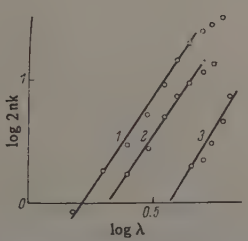

Fig. 5. 1—N = 12.1 × 10^{20} cm^{-3}; 2—N = 6.55 × 10^{20} cm^{-3}; 3—N = 1.32 × 10^{20} cm^{-3}.

By using the relation $\mu = e\tau/m'$ one can calculate electron mobility from the values of τ and m′ known the optical measurements. Figure 6 shows that the ron mobility varies within the limits 2-42 cm^2/volt-sec and increases as the carrier concentration decreases. On the basis of the way in which mobility varies with N it may be supposed that the mobility is due chiefly to scattering of electrons from positive ions of excess cadmium, while scattering at thermal fluctuations plays a small role in the case of large concentrations under consideration here.

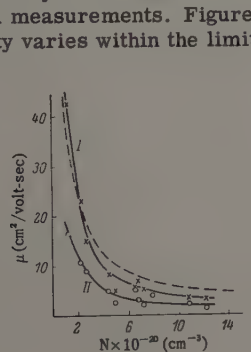

Fig. 6

The theoretical dependence of relaxation time on the impurity ion concentration N_i in a semiconductor is given by the familiar Conwell-Weisskopf formula derived under classical assumptions. The Conwell-Weisskopf relation can be used to calculate the mobility of degenerate semiconductors:

$$\mu = \frac{4ea_i}{\pi p_f} \frac{\left(\frac{2E_f}{E_i}\right)^2}{2\ln\left[1+\left(\frac{2E_f}{E_i}\right)^2\right]}. \qquad (9)$$

Here $p_F = (h/2)(3N/\pi)^{1/3}$, $E_F \approx (h^2/8m')(3N/\pi)^{2/3}$, $a_i = N_i^{-1/3}$, $E_i = 2e^2/\varepsilon a_i$, where ε is the dielectric constant of the substance. The calculation assumes that $N_i = N$, i.e., with each impurity ion is associated a single electron. Furthermore ε is taken equal to ε_0, since in our case the experimental value of the collision frequency ν_F is greater than the frequency of optical lattice vibrations. In other words, during the relaxation time only the electron shells at lattice points of the crystal are polarized. The theoretical curve (the dashed line of Fig. 6) is in good agreement with the experimental curve (curve I) particularly in the region of small concentrations. In the region of large concentrations the experimental points lie below the theoretical curve, indicating the existence of an additional source of scattering. The mobility found from measurements of electrical conductivity in static fields ($\mu = R\sigma$ where R is the Hall constant, and σ is the electrical conductivity) also diminishes as the carrier concentration increases. However, the experimental curve (curve II) lies considerably below the theoretical curve. This last result is apparently explained by the inhomogeneity of the crystal layers associated with the presence of high-resistance transition layers between grains of crystalline CdO. In static fields these transition layers are an additional source of electron scattering.

In conclusion the authors wish to express their thanks to I. N. Shklyarevskii and N. A. Vlasenko for their interest in the work and for a discussion.

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ON THE ROLE OF DIMENSIONAL LIMITATIONS OF TOTAL REFLECTION RESONANC FILTERS

L. V. Iogansen (pp. 542-546)

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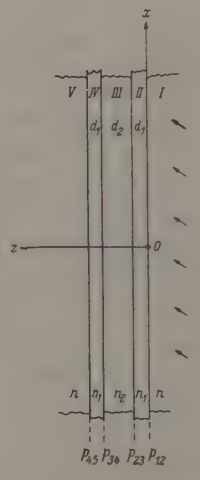
It is shown that in filters which use total internal reflection an important role is played by the linear dimensions of the filter, which up to now had not been considered. A theory of the flow of limited waves through the filter is developed, which permits calculation of the transparency of filters of finite dimensions. The results of this theory are in agreement with the available experimental data, while the older theory contradicts the experiments and makes an attempt to explain the discrepancy solely by the presence of nonhomogeneities in thin dielectric films.

In 1947 an optical filter was proposed, which utilizes the phenomenon of total reflection.[1] The illustration shows the cross section of this filter. It is composed of two identical films II and IV with a small refraction index n_1, giving total internal reflection. The border media I and V and the inner layer III possess similar indices of refraction n and n_2, such that $n \simeq n_2 \gg n_1$. If it is assumed that light absorption is nonexistent in the medium, such a filter, according to existing calculations,[2] should be totally transparent for the resonance wavelength. In addition to this the width of the band of transmission may be made narrow by increasing the thickness d_1 of the totally reflecting layers. It was expected that filters possessing such convenient properties would find wide use in optics, especially in the far infrared and in the microwave region. However, many experiments on utilization of such filters have shown that in reality they do not possess the indicated properties.[3,4] The filters prepared for infrared and microwave regions were totally nontransparent. The optical filters could be made. But it was shown that when d_1 was increased from $(3/4)\lambda$ to $(5/4)\lambda$ (λ = wavelength of light) the transparency of the filter decreased to zero, while the width of the transmission band did not decrease. An increase in the thickness d_2 of the inner layer III also leads to a decrease in the transparency of filter. Up to now, this disagreement between theory and experiment was explained by the presence of nonhomogeneities in thin dielectric films. It was assumed that the nonhomogeneities increase with increasing thickness of the film and lead to a loss of transparency of the filter.[3-5] On the basis of this theory, methods of measurements of nonhomogeneities in films based on the transparency of a filter[6] were worked out.

In this work we have shown that the disagreement of the earlier theory and experiment is not caused by the defects of the films but by the shortcomings of the earlier theory. This theory is justified only in the case of infinitely extensive filters and plane waves unlimited in space. In practice, the surfaces of the filter and the waves are always finite. The presence of finite limits of extent determines and causes the inapplicability of the earlier theory in spite of the fact that the dimensions of



the filter are usually larger by several orders of mag tude than the thickness of the films.

Let us first consider qualitatively the physical si of this phenomenon. It is usually forgotten that the ab solute transparency of the filter is associated with th phenomenon of resonance, because of which the ampli tude of the waves in the inner layer III becomes large than the amplitude of the incident wave by a factor of $\exp(q_z d_1)$ (q_1 is the value of the imaginary component the wave vector in the film with total reflection). Let consider a filter of infinite extent. Let us assume tha an unlimited plane monocromatic wave is falling fron the medium I onto the boundary surface P_{12}, the wave having positive components of the wave vector $k_x > 0$ and $k_z > 0$ and a given amplitude A_1. In the case of resonance a flow of energy condensed in the inner lay III occurs along the layer in the direction of increasi x. In this case the order of magnitude of the density the flow of energy is larger by a factor of $\exp(2q_2 d_1)$ the corresponding value for the decreasing wave. Th total flow of energy along the inner layer III is propo tional to $d_2 \exp(2q_z d_1)$. Let us assume now that the bo

urface P_{12} (in our case the surface $z = 0$) in the
n $x < 0$ is totally nontransparent. In this case in
ner layer III, in the region $x < 0$, there will be no
s. As one moves to the region $x > 0$ the amplitude
waves in the inner layer III will increase gradually.
total energy incident on the filter reached the in-
f the inner layer III and did not flow out of it through
he amplitude of the waves in the inner layer III
reach, under these idealized conditions, the reso-
value close to

$$x_0 = d_2 \exp(2q_z d_1). \qquad (1)$$

Actually this will occur only when $x \gg x_0$. Conse-
ly, the resonance passage of waves through the fil-
possible only when the linear dimensions of the
L are large in comparison with x_0, i.e., $L \gg x_0$.
crease in d_2 and especially in d_1 leads to a rapid
ase of x_0 and as a result of this, the condition
x_0 is not maintained and a loss of filter transpar-
occurs.

We give below an approximate method of quantita-
alculation of this phenomena using "orthogonal
." We shall describe the waves by the vector po-
l **A**(x, y, z, t), the electric field $\mathbf{E} = -(1/c)\mathbf{A}$, and
agnetic field $\mathbf{H} = [\nabla \mathbf{A}]$ (it is assumed that the me-
is nonmagnetic). We shall limit ourselves to the
of s-polarization, when the electric field of the wave
ected along a unit vector **s** in the direction of the
s in the plane of the boundary, we shall consider the
ations produced, and we shall consider the condi-
along the y-axis as uniform. In this case $\mathbf{A}(x, y, z) = \mathbf{s}A(x, z)\exp(i\omega t)$, where $A(x, z)$ is the solution of
o dimensional Helmholtz equation:

$$\frac{\partial^2 A}{\partial x^2} + \frac{\partial^2 A}{\partial z^2} + \left(\frac{n\omega}{c}\right)^2 A = 0. \qquad (2)$$

Let us write the approximate solutions of Eq. (2), which will help us to solve the problem. In the region I

$$A(x, z) = A\left(x - \frac{k_x}{k_z} z\right) \exp[-i(k_x x + k_z z)]$$

$$B\left(x + \frac{k_x}{k_z} z\right) \exp[-i(k_x x - k_z z)], \qquad (3)$$

In the region II

$$A(x, z) = F\left(x + i\frac{k_x}{q_z} z\right) \exp[-i(k_x x + iq_z z)] + G\left(x - i\frac{k_x}{q_z} z\right) \times \exp[-i(k_x x - iq_z z)]. \qquad (4)$$

Here

$$k_x^2 + k_z^2 = \left(\frac{n\omega}{c}\right)^2, \quad k_x^2 - q_z^2 = \left(\frac{n_1\omega}{c}\right)^2;$$

A, B, F, G are complex amplitudes which are arbitrary functions of their arguments, and do not change considerably in a distance equal to a wavelength (i.e., $\partial B/\partial x \ll k_x B$, $\partial B/\partial z \ll k_z B$, etc.). The approximate solutions (3) and (4) will be called "orthogonal waves," in order to reflect the fact that the planes in which the complex amplitudes and phases are constant are orthogonal. The usual boundary conditions of the fusing of the fields in the boundary plane P_{12} lead to the following differential relationships between amplitudes:

$$A(x) + B(x) = F(x) + G(x), \qquad (5)$$

$$A(x) - B(x) - i\frac{k_x}{k_z^2}[A'(x) - B'(x)] = i\frac{q_z}{k_z}[F(x) - G(x)] - \frac{k_x}{k_z q_z}[F'(x) - G'(x)]. \qquad (6)$$

These differential equations are generalized forms of the usual algebraic relationships between constant amplitudes. Disregarding second derivatives, the system of equations (5) and (6) may be solved for A(x) and B(x) or F(x) and G(x) as follows:

$$\left.\begin{aligned} A &= \frac{1}{2}\left(1 + i\frac{q_z}{k_z}\right)F + \frac{1}{2}\left(1 - i\frac{q_z}{k_z}\right)G - \frac{1}{2}\frac{k_x}{q_z k_z}\left(1 + \frac{q_z^2}{k_z^2}\right)(F' - G'), \\ B &= \frac{1}{2}\left(1 - i\frac{q_z}{k_z}\right)F + \frac{1}{2}\left(1 + i\frac{q_z}{k_z}\right)G + \frac{1}{2}\frac{k_x}{q_z k_z}\left(1 + \frac{q_z^2}{k_z^2}\right)(F' - G'); \end{aligned}\right\} \qquad (7)$$

$$\left.\begin{aligned} F &= \frac{1}{2}\left(1 - i\frac{k_z}{q_z}\right)A + \frac{1}{2}\left(1 + i\frac{k_z}{q_z}\right)B - \frac{1}{2}\frac{k_x}{q_z k_z}\left(1 + \frac{k_z^2}{q_z^2}\right)(A' - B'), \\ G &= \frac{1}{2}\left(1 + i\frac{k_z}{q_z}\right)A + \frac{1}{2}\left(1 - i\frac{k_z}{q_z}\right)B + \frac{1}{2}\frac{k_x}{q_z k_z}\left(1 + \frac{k_z^2}{q_z^2}\right)(A' - B'). \end{aligned}\right\} \qquad (8)$$

Using Eqs. (7) and (8), finite filters with total interflection may be calculated. As an example we shall der a semi-infinite filter, for which we have quali-ly worked out the above processes. As before, we consider that from the medium I an infinite plane with a given amplitude A_1 and positive components ve vector $k_x > 0$ and $k_z > 0$ falls on the plane P_{12} h is nontransparent in the region $x < 0$). On the side of the filter in the medium V we shall have the wave which passes through; therefore, on the dary P_{45} we have $B_{P_{45}}(x) \equiv 0$, $A_{P_{45}}(x) = A(x)$. Here is the desired amplitude of the wave which passed gh the filter. From the physical considerations above, if follows that when $x \to 0$, $A(x) \to 0$, and $x \to \infty$, $A(x)$ approaches the known value for the in- filter. In order to find the amplitudes of the waves e other side of the boundary plane P_{45} in the totally cting inner layer IV, we will substitute $A_{P_{45}}(x)$ and $B_{P_{45}}(x)$ into Eq. (8) and obtain:

$$\left.\begin{aligned} F_{P_{45}}(x) &= \frac{1}{2}\left(1 - i\frac{k_x}{q_z}\right)A(x) - \frac{1}{2}\frac{k_x}{q_z k_z}\left(1 + \frac{k_z^2}{q_z^2}\right)A'(x), \\ G_{P_{45}}(x) &= \frac{1}{2}\left(1 + i\frac{k_x}{q_z}\right)A(x) + \frac{1}{2}\frac{k_x}{q_z k_z}\left(1 + \frac{k_z^2}{q_z^2}\right)A'(x). \end{aligned}\right\} \qquad (9)$$

These equations express the unknown functions $F_{P_{45}}(x)$ and $G_{P_{45}}(x)$ in terms of the desired function A_x and its derivative. We shall now express the amplitudes of the waves on the boundary P_{34} in the layer IV, using their value on the boundary P_{45}. For this we use Eq. (4), where we must put $z = -d_1$, and obtain:

$$F_{P_{34}}(x) = F_{P_{45}}\left(x - i\frac{k_x}{q_z} d_1\right) \cdot \exp(-q_z d_1),$$

$$G_{P_{34}}(x) = G_{P_{45}}\left(x + i\frac{k_x}{q_z} d_1\right) \cdot \exp(q_z d_1).$$

Utilizing the condition of slow changes of amplitudes

and the fact that usually $d_1 \sim d_2 \sim \lambda$, one may break the amplitudes into series according to the degrees of d_1 and use only the first two members:

$$F_{P_{34}}(x) = \left[F_{P_{34}}(x) - i \frac{k_z}{k_z} d_1 F'_{P_{34}}(x) \right] \exp(-q_z d_1),$$

$$G_{P_{34}}(x) = \left[G_{P_{34}}(x) + i \frac{k_z}{k_z} d_1 G'_{P_{34}}(x) \right] \exp(q_z d_1).$$

Substituting Eqs. (9) into these equations and disregarding second derivatives, we obtain the following expression for the unknown amplitudes $F_{P34}(x)$ and $G_{P34}(x)$ in terms of the desired function A_x and its derivative:

$$\left.\begin{aligned} F_{P_{34}}(x) &= \left\{ \frac{1}{2}\left(1 - i\frac{k_z}{q_z}\right) A(x) - \frac{1}{2}\frac{k_x}{k_z}\left[\frac{1}{q_z}\left(1 + \frac{k_x^2}{q_z^2}\right) \right.\right. \\ &\quad \left.\left. + i d_1 \left(1 - i\frac{k_z}{q_z}\right)\right] A'(x) \right\} \exp(-q_z d_1), \\ G_{P_{34}}(x) &= \left\{ \frac{1}{2}\left(1 + i\frac{k_z}{q_z}\right) A(x) + \frac{1}{2}\frac{k_x}{k_z}\left[\frac{1}{q_z}\left(1 + \frac{k_x^2}{q_z^2}\right) \right.\right. \\ &\quad \left.\left. + i d_1 \left(1 + i\frac{k_z}{q_z}\right)\right] A'(x) \right\} \exp(q_z d_1). \end{aligned}\right\} \quad (10)$$

Furthermore, in order to find the amplitudes of the waves on the boundary P_{34} in the layer III, it is necessary to substitute Eq. (10) into Eq. (7), etc., repeating the above operations as many times as there are boundaries and inner layers. As a result we will obtain amplitudes of waves $A_{P_{12}}$ and $B_{P_{12}}$ in the medium I on the boundary P_{12} which will be expressed in terms of A_x and A'_x. But $A_{P_{12}}(x) \equiv A_I$ is the given constant amplitude of the incident wave. Therefore it is possible to determine A_x from the differential equation and then, going backwards, determine all the other amplitudes. In the general case the calculation is extremely tedius. We shall now consider the simplest case, when $n_2 = n$ and $k_z = q_z$. We shall consider that the exact resonance condition is fulfilled, which in this case takes the simple form $\tan(k_z d_2) = \pm\infty$. Performing the calculation according to the above indicated method, we obtain:

$$A_I = -iA(x) - il_0 \cdot A'(x), \quad (11)$$

$$B_{P_{12}}(x) = l_0 \cdot A'(x), \quad (12)$$

where the characteristic length

$$l_0 = \frac{k_x}{2k_z}\left(d_2 + \frac{2}{q_z}\right)\exp(2q_z d_1). \quad (13)$$

has been introduced.

For Eq. (11) the desired solution, valid in the region where $x > 0$ and satisfying the above-mentioned conditions at 0 and at infinity, is:

$$A(x) = iA_I\left[1 - \exp\left(-\frac{x}{l_0}\right)\right]. \quad (14)$$

Substituting Eq. (14) into Eq. (12), we obtain:

$$B_{P_{12}}(x) = iA_I \cdot \exp\left(-\frac{x}{l_0}\right).$$

The characteristic length l_0 corresponds to the lengt (1) obtained above from qualitative reasoning. The pr ence of the sum $[d_2 + (2/q_z)]$ in Eq. (13) in place of d_2 in Eq. (1) is caused by the fact that accumulation of e ergy occurs not only in layer III but also in neighbori regions of thickness $(1/q_z)$ in the totally reflecting layers II and IV.

The local transparency of the filter is $T(x) = |A(x)|^2/|A_I|^2$. From Eq. (14) it follows that

$$T(x) = \left[1 - \exp\left(-\frac{x}{l_0}\right)\right]^2$$

In the limit $x \gg l_0$, $T = 1$, as it should be in the c of exact resonance for an infinite filter. The average transparency of the filter having the dimensions L al the axis x is

$$\bar{T} = \frac{1}{L}\int_0^L T(x)\,dx.$$

From this it is easy to derive that when $L \gg l_0$, $\bar{T} \cong 1 - (3/2)(l_0/L)$, and when $L \ll l_0$, $\bar{T} \cong (1/3)(L/l_0)^2$.

In conclusion we shall cite a numerical example an illustration of the practical significance of this phe nomenon.

Let us assume $n = 2$, $n_1 = 1.41$, angle of incidenc $\varphi = 60°$. In this case $k_x = \sqrt{3}(2\pi/\lambda)$, $k_z = q_z = 2\pi/\lambda$. Le $\lambda = 0.6\ \mu$. For $d_1 = (3/4)\lambda$, $d_2 = (5/4)\lambda$, we obtain $l_0 =$ cm. For $d_1 = (5/4)\lambda$, $d_2 = (5/4)\lambda$, we obtain $l_0 = 10$ meters.

If a conventional filter with $L \cong 10$ cm is taken, i the first case we shall obtain high transparency, and the second case we will have an almost nontransparer filter. This is what happens in practice.[3,4]

I wish to express my gratitude to E. V. Shpol'ski for his support and interest in this work and to V. L. Ginzburg for useful discussion of the results obtained

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NVARIANCE OF MAXWELL'S EQUATIONS AND THE PRINCIPLES OF REVERSIBILITY FOR A PLANE HARMONIC WAVE

L. Dunaisky (pp. 547-549)
Brno University, Czechoslovakia

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Kard, in an as yet unpublished paper, relates identi- obtained by him earlier[1] with the invariance of Max- 's equations. These identities were given by him in orm:

$$r_R\tilde{r}_R^* + t_R\tilde{t}_L^* = 1, \tag{1}$$

$$r_R\tilde{t}_R^* + t_R\tilde{r}_L^* = 0, \tag{2}$$

re the symbol ~ denotes the conjugate layer. Kard es the question of reversibility with the invariance axwell's equations. The purpose of this paper is the detailed investigation of the questions raised and explanation of the physical meaning of conjugate rings.

Maxwell's equations for a plane harmonic wave can t in the form*:

ot over a vector denotes differentiation with respect me. Complex quantities are denoted by heavy italics, rs by roman type.

$Z_v = \sqrt{\mu_v/\varepsilon_v}$—wave impedance in vacuo.

$$Z_0\mathbf{H} \times \mathbf{m} = \varepsilon_{r1}\dot{\mathbf{E}} - t\varepsilon_{r2}\mathbf{E}, \tag{3}$$

$$\mathbf{m} \times \mathbf{E} = Z_0\dot{\mathbf{H}}, \tag{4}$$

$$\mathbf{m} \cdot \mathbf{E} = 0, \tag{5}$$

$$\mathbf{m} \cdot \mathbf{H} = 0. \tag{6}$$

Amongst these quantities there exist the relations

$$\mathbf{m}^2 = (\mathbf{m}_1 - i\mathbf{m}_2)^2 = \varepsilon_r = \varepsilon_{r1} - t\varepsilon_{r2} = \frac{t}{\varepsilon_0} - \frac{\sigma}{\varepsilon_0\omega}. \tag{7}$$

The vector $\mathbf{m}_1$ is perpendicular to the plane of con- phase, and $\mathbf{m}_2$ is perpendicular to the plane of con- amplitude. Moreover, the moduli of these vectors onstant for the oblique angle of incidence introduced ašíček (the vectors of refraction were introduced by rov[5]).

Equations (3)-(6) are invariant with respect to the types of transformations shown in the table. For sformations of type a and b it is necessary, of se, to change the signs of the dotted quantities also. sons for which it is necessary to distinguish between sformations of type a and b (and, similarly, c and e given in ref. 2. Transformations in the last column defined on the basis that

$$x = \frac{2\pi}{\lambda}\,\mathbf{m} \cdot \mathbf{d}, \tag{8}$$

e **d** is the thickness vector of the layer.*

e modulus of this vector is equal to the thickness of ayer. This vector is perpendicular to the boundary eparation and oriented in the direction of propagation e wave (cf. figure).

Invariance and Reversibility Principles
(t—time, m—refraction vector[5])

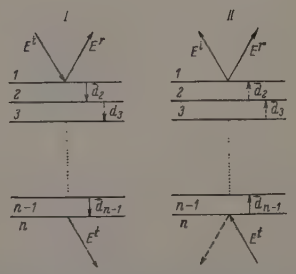
Type of transformation	Quantity which must be changed					
	t	E	H	σ	m	x
a	$-t$	E	$-$H	$-\sigma$	m	$-x$
b	$-t$	$-$E	H	$-\sigma$	m	$-x$
c	t	E*	$-$H*	$-\sigma$	$-$m*	x^*
d	t	$-$E*	H*	$-\sigma$	$-$m*	x^*

For each of the invariances it is necessary to make the transformation $\mathbf{d} \to -\mathbf{d}$, since the wave propagates in the opposite direction. For invariances of type a and b we get for an arbitrarily polarized wave at normal incidence, the following relations for the components:

$$r_R E^r + t_L E^i = r_R r_R E^i + t_L t_R E^i = E^i, \tag{9}$$

$$t_D E^r + r_L E^i = t_R r_R E^i + r_L t_R E^i = 0. \tag{10}$$

These relations are valid for an arbitrary system of plane parallel layers.



Schematic of a many-layered coating. I—Before applying reversibility; II—after applying reversibility. The superscripts i, r, and t denote incident, reflected, and refracted waves, respectively.

The symbol ~ underneath means that the amplitude coefficients for a simple boundary of separation should be left unchanged and the sign of x changed. The meaning of the other symbols is clear from the figure.

From the last two relations the relations (1) and (2) follow if we make use of the symbolic equation

$$\tilde{}^* \equiv _. \tag{11}$$

Making use of the invariances c and d, we get the following relations:

$$r'_R r^*_R + t'_L t^*_R = 1, \tag{12}$$

$$t'_R r^*_R + r'_L t^*_R = 0. \tag{13}$$

The dash means that the amplitude components for a simple boundary of separation and the quantity x

should be replaced by complex conjugate quantities. These relations also lead to the relations (1) and (2). From the preceding it follows that besides the invariances given by Kard, there exist three more types of invariances leading to the same relations.*

*Independently of Kard, relations (1) and (2) were also obtained by Shantavy. His work was published in the journal Optica Acta.

We now come to the question of reversibility. Processes are reversible only when they occur without damping, i.e., when their electromagnetic energy is not changed into heat. Processes in which there is damping are irreversible (cf., for example, refs. 2-4).

The invariances shown in the table are equivalent to the principle of reversibility* (at least in the thermodynamic sense) only when there is no damping. This takes place only in two cases: (1) $\sigma = 0$ (dielectric) and (2) in the presence of an arbitrary simple (Fresnel's) boundary of separation. The difference between these two cases lies in the fact that for a simple boundary of separation, when at least one of the media is a metal, the principle of reversibility can be applied only to an infinitesimally small neighborhood of the boundary of separation in an infinitesimally small time interval, whereas for a dielectric the principle of reversibility is fulfilled for an arbitrary volume and interval of time.

*In every invariance we are talking about the reversibility of processes. However, from our point of view we can speak of the principle of reversibility only in the absence of damping.

After appropriate transformations we obtain med which Kard called conjugate. Physically this means t in these media there is complete self-conversion of h into electromagnetic energy. Such a process obviousl contradicts the second law of thermodynamics. Never theless on the basis of such a method we obtain the co rect relations (1) and (2). This phenomenon can be ex plained on the basis of the statistical interpretation o the second law of thermodynamics. In other words, th exists a very small probability that a real coating sha behave so that its conductance shall be negative, i.e., a conjugate coating.

This work arose out of the author's discussion of this subject with Shantavy and Knittl in connection wit a defense by the latter of a dissertation for candidacy and also on the basis of a discussion between Vašíček and Kard.

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MEASUREMENT OF THE DIAMETER OF THE HIGH-PRESSURE PULSE DISCHARGE CHANNEL IN VARIOUS SPECTRAL REGIONS

K. S. Vul'fson and F. A. Charnaya (pp. 549-551)

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In high-pressure pulse lamps working with sufficiently high energy concentration in the discharge channel, the absorbance of the plasma in the channel is close to unity.[1-6] Investigations have shown that for obtaining high absorbance in the plasma, less concentration of energy is needed in the long wavelength range than in the short wavelength range.[1,2] This relationship, which is in agreement with theoretical considerations,[7,8] means that a given value of the absorption coefficient is obtained in the long wavelength emission at lower temperatures. It should be expected therefore that, because of the considerable temperature gradient in the outer regions of the channel, the diameter observed in the long wavelength emission will be larger than that in the short wavelength emission. The purpose of this work is the experimental test of this supposition.

In spite of a considerable number of papers dedicated to the investigation of the broadening of the pulse discharge channel,[9-13] it was only in one paper[13] that a comparison was made of the development of the broadening of the channel in two spectral regions separated by blue and infrared light filters. The results of this comparison have demonstrated a considerable difference between the short and the long wavelength emission in the later stages of the channel development. However, the auth did not find the expected effect in the early stages of emission which correspond to the highest values of te perature and brightness, and concluded that the speed propagation of the luminous front is equal in both spe tral regions.

In contrast to the widely known schemes for the ror time sweep,[9-15] the optical arrangement used in t present work permits the observation of the broadeni of the diameter of the channel in spectrally dispersed light (Fig. 1). The discharge channel of the pulse lam is projected by means of an achromatic objective len on the plane of the entrance slit of the monochromato (the projection of the discharge axis being perpendicu to the entrance slit of the monochromator). The imag the region of the channel projection cut out by the ent slit is obtained in the plane of the exit slit of the mon chromator. The time sweep is carried out by a rotat objective mirror 6, which projects the exit slit of the monochromator onto the plane of the photographic pl 8 situated in the camera 7. The plane mirror 5 perm a substantial reduction of the angle between the light and the optical axis, which results in a considerable crease of aberration distortions. Since, for technica

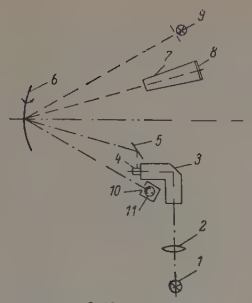

Fig. 1. Diagram of the optical arrangement.

ns, it was convenient to have the rotation axis of oncave mirror in a horizontal plane, it was neces- to correspondingly rotate the image of the vertical the monochromator. For this purpose, a twin 4 was used.

he synchronization of the position of the rotating ive mirror with the beginning of the discharge was plished by an optical method: a narrow horizontal luminated by a small light bulb 9 is projected by the ive 6 onto a horizontal slit 10 cut out in a hous- a photoelement 11. The photocurrent pulse which s when the two slits are superimposed is amplified d to the control system of the pulse lamp. The time ution of the arrangement was 7×10^6 sec^{-1}, the of the monochromator slits, 0.05-0.08 mm. The graphic film of high sensitivity Panchrom type X sed.

he diameter of the channel was determined from me-sweep photographs, not by visual measure- [9-13] which are very inaccurate, but by photographic metry. The exposure markers were made with a filter for each wavelength measured. The time- photographs were measured photometrically in rection perpendicular to the time axis along the sections at a distance of 0.1 μsec from each other. the data obtained the distribution curves were for the spectral density of the radiative bright- B_λ) in the direction of the normal to the discharge across the channel) for various times. Figure 2 de- he characteristic curves of the distribution B_λ ual to unity at the maximum. For the presentation we have assumed that the diameter of the chan- equal to the distance between those points of the bution curves B_λ, where the value of B_λ is one f the maximum value.

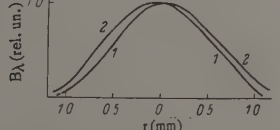

Fig. 2. Distribution of the spectral density of the radiative brightness of argon lamps in the direction perpendicular to the axis of the discharge 0.2 μsec after its initiation. Discharge conditions: p = 18 atm; C = 0.6 μf; U = kv; λ(μ): curve 1—0.4; curve 2—0.66.

he measurement of the diameter of the channel is ered by the fact that the time-resolved broadening channel is not exactly reproducible in various s, because of the spacial instability of the channel. fore, for each wavelength, from 7 to 10 time-sweep photographs were made which were measured by the above-described method, and then the results of photometric measurements for each cross section were averaged. Control experiments have shown that, as a result of averaging made with two series of four and five time-sweep photographs, exactly coinciding curves for each wavelength are obtained. It should also be mentioned that for the initial stages of the channel development ($t < 1$ μsec) which are of the greatest interest, the differences between the various sweep photographs are considerably smaller than for the following stages. The photometric evaluation of the time-sweep photographs of the channel diameter used in the present investigation, and also the averaging of a large number of data from separate experiments, justifies the statement that the difference found for the diameters of the channel is outside the limits of the experimental errors.

Figure 3 shows the dependence of the diameter of the channel on time as obtained with the wavelengths $\lambda = 0.4$ and 0.66 μ for argon, krypton, and xenon lamps. Inspection of these curves shows that in all three gases the diameter of the channel is larger in the longer wavelength emission than in the shorter wavelength emission. The above curves depicting the dependence of the diameter of the channel on the wavelength indicate that the luminous surface which determines the diameter of the channel in the short wavelength emission is closer to the discharge axis than that in the long wavelength emission, and is, therefore, in the region of higher temperatures.

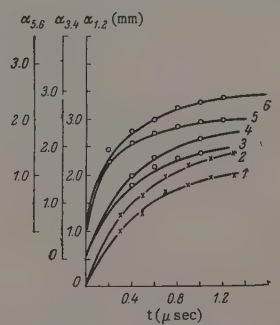

Fig. 3. Dependence of the channel diameter on time for various lamps. Gas: curves 1, 2—xenon; curves 3, 4—krypton; curves 5, 6—argon. λ(μ): curves 1, 3, 5—0.4; curves 2, 4, 6—0.66. For discharge conditions see legend of Fig. 2.

The established effect of the dependence of the channel diameter on the wavelength is of fundamental significance, because on the one hand, it confirms the fact that the saturation of the brightness is caused by high absorption of the channel plasma, and, on the other hand, it permits, in combination with the measurements of B_λ, obtaining data on the radial temperature gradient.

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ON THE INFRARED ABSORPTION SPECTRA OF HYDROGEN IN SOLUTIONS

M. O. Bulanin and N. D. Orlova (pp. 551-553)

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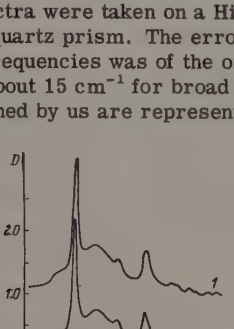
Intermolecular interaction leads to the appearance of a vibration-rotation infrared absorption spectrum which is forbidden for symmetric diatomic molecules; this spectrum has selection rules which are analogous to the selection rules for Raman spectra.[1] The theory of this so-called induced absorption, which was predicted by Condon,[2] has been developed in the works of van Kranendonk.[3] Since the very existence of induced spectra is brought about by the action of intermolecular forces, the investigation of these spectra opens new possibilities for studying the properties of the intermolecular field and molecular motion in liquid media.

The large value of the rotational constant and the simplicity of the hydrogen molecule make it especially favorable for the study of perturbations in vibration-rotation spectra. Up to the present time, induced absorption has been investigated only in pure gaseous hydrogen and its mixtures with foreign gases,[1,4-6] as well as in liquid and crystalline hydrogen.[7] In the present work, we set forth the results of an investigation which we have undertaken on the induced infrared spectra of hydrogen in solutions.

Spectra were obtained for solutions of hydrogen in CCl_4 and $CFCl_2$-CF_2Cl. The solutions were prepared in a steel cell with fused quartz windows. The hydrogen was introduced into the cell under pressure of 15-100 kg/cm^2. The spectra were taken on a Hilger H-800 spectrometer with a quartz prism. The error in the determination of the frequencies was of the order of 5 cm^{-1} for narrow and about 15 cm^{-1} for broad bands. Two of the spectra obtained by us are represented in the figure.



Absorption spectra of hydrogen in solutions at room temperature. Solvent and pressure (kg/cm^2): Curve 1—$C_2Cl_3F_3$, 75; curve 2—CCl_4, 95. Layer thickness 9 cm.

Frequencies and Interpretation of the Absorption Bands in the Infrared Spectrum of Hydrogen

ν (cm⁻¹)			Interpretation
Free molecules H_2*	Solution in CCl_4	Solution in $C_2F_3Cl_3$	
—	3950	4000	Q_P
4155	4131	4138	Q_Q
—	4315	4300	Q_R
4501	4470	4480	$S(0)$
4721	4695	4700	$S(1)$
			$\nu_{H_2}(Q_Q) + \nu_{CCl_4}$**
—	4905	—	4131 + 768 = 4899
—	4935	—	4131 + 797 = 4927
—	5100	—	4131 + 982 = 5113
			$\nu_{H_2}(Q_Q) + \nu_{C_2Cl_3F_3}$***
—	—	4905	?
—	—	4965	4138 + 811 = 4949
—	—	5050	4138 + 908 = 5046
—	—	5100	?
—	—	5200	4138 + 1047 = 5185
—	—	5270	4138 + 1113 = 5251

*According to ref. 8.
**According to Herzberg's data.[10]
***According to our measurements.

In the table are presented the frequency values and interpretation of the observed absorption bands.

The vibration-rotation spectrum of hydrogen at peratures which are not too high consists of Q and branches, corresponding to transitions with a chang the rotational quantum number of $\Delta J = 0$ and $\Delta J =$ spectively. Now, for normal hydrogen, only the zer and first vibrational levels are significantly populat Therefore, the components Q(0) ($J = 0 \rightarrow J = 0$) and ($J = 1 \rightarrow J = 1$), which are not usually resolved in th infrared spectrum, enter into the Q branch, and the ponents S(0) ($J = 0 \rightarrow J = 2$) and S(1) ($J = 1 \rightarrow J =$ the S branch. In the induced spectrum, the Q bran consists of three bands, designated as Q_P, Q_Q, and Of these, Q_Q corresponds to the purely vibrational tion and Q_P and Q_R to vibrational transitions which accompanied by a change in the kinetic energy of th molecules. In the case of the Q_P band, the energy light quantum does not suffice to excite the vibratio and this insufficiency is made up at the expense of kinetic energy of the molecule. In the Q_R band, on contrary, the energy of the quantum is also expende an increase in the kinetic energy. The position and of the Q_P and Q_R bands depend on the temperature

, and nature of the interacting molecules.

In the hydrogen solution spectra obtained in the ent work, the absorption band at 4135 cm^{-1}, with d wings on both sides, is the most intense. Compari- with the induced spectrum of gaseous hydrogen al- us to interpret this band as Q_Q and the wings as the nd Q_R bands. The bands around 4500 and 4700 cm^{-1} be correspondingly ascribed to the S(0) and S(1) sitions. With such an assignment of the absorption s in the spectrum of dissolved hydrogen, the values eir frequencies are close to the frequencies for ous hydrogen.[8] The observed band shift in the solu- by approximately 20 cm^{-1} toward shorter wave- lhs, somewhat larger in CCl_4 than in $C_2F_3Cl_3$, is ably explained by the polarizing action of the solvent. oing from one solvent to another, the relative inten- s of the different components of the vibrational band drogen are almost unchanged.

The presence of distinct Q(0), S(1), and S(0) bands e spectrum shows that, in the solutions studied, are H_2 molecules in various rotational states; i.e., ner words, that the rotational motion of the hydro- molecules is relatively little perturbed. In contrast e spectrum of liquid hydrogen,[7] the Q_Q component is intense in the solution spectra than the components e S branch. Evidently the restriction of the rotational on of the hydrogen molecules is greater in the solu- on account of the more active environment. As a equence, a large fraction of the molecules undergo rational transition without change in the rotational

The spectrum in the frequency region 4900 cm^{-1} and e depends substantially on the solvent. This may be preted by assuming that the observed bands corre- to so-called simultaneous transitions;[1,9] i.e., to multaneous vibrational excitation of two molecules— hydrogen and solvent. Such transitions lead to the appearance of bands in the spectrum at frequencies approximately equal to the sum (and, under favorable conditions, to the difference also) of the vibrational frequencies of the separate components of the mixture. As can be seen from the table, the frequencies of almost all the bands present in the spectra of hydrogen solutions in the region $\nu > 4900$ cm^{-1} are in satisfactory agreement with sums of the vibration frequencies of hydrogen molecules and solvent molecules.

The authors thank V. M. Chulanovskii for his constant interest and for discussion of the results of the work.

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THE USE OF REFLECTED LIGHT IN WORK WITH A FABRY-PEROT ETALON

V. I. Odintsov (pp. 553-555)

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When light falls onto a Fabry-Perot etalon at differ- ngles of incidence, most of it (usually more than is reflected back by the etalon towards the light e. This reflected light can be again directed to- the etalon if a spherical mirror is placed behind ght source in such a way that its center of curva- ies in the focal plane of the condensing lens in front etalon (see the diagram, where 1 is the light e, 2 is the condensing lens, 3 is the Fabry-Perot a, 4 is the spherical mirror, 5 is the objective projects the interference pattern onto the spectro- slit S, and F is the focal plane of the lens 2),*

tup with a spherical mirror behind the light source sed in atomic beam sources[1,2] in order to increase tensity by the amount of light emitted by the source opposite direction, namely, towards the mirror. ver, the role of the light reflected by the Fabry- etalon was not considered there.

Consider in the focal plane F* the points A, A_1, A_2, A_3,... chosen in such a way that a beam of light originating at A_1, after reflections at the etalon 3 and the spherical mirror 4, passes through the point A, while a beam of light originating at A_2, after the same reflections, passes through the point A_1, etc. Let the point O in the focal plane F be the point corresponding to the center of the interference pattern and let the point C, also in the plane F, be the center of curvature of the spherical mirror. It is easy to satisfy oneself that the points A, A_1, A_2,... lie on a straight line parallel to the line OC and at a distance from one another equal to twice the distance between the points O and C. Let τ_1 be the coefficient specifying the reduction in intensity of the monochromatic light which arrived at the point A from the point A_1, let τ_2 be the reduction coefficient for light arriving at point

*The case in which the light source fills a volume is not important here.

A_1 from point A_2, etc. It is obvious that light leaving every point A_1 in the direction of the etalon will, after a series of consecutive reflections at the etalon and at the spherical mirror, pass through the point A towards the etalon. Hence the intensity at the point in the interference pattern corresponding to the point A will be equal to

$$B = B_0(1 + \tau_1 + \tau_1\tau_2 + \tau_1\tau_2\tau_3 + \ldots) = B_0 k.$$

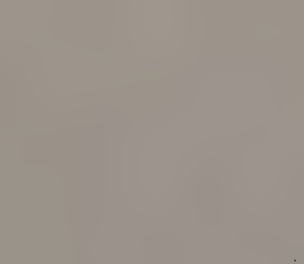
Here B_0 is the intensity of the interference pattern obtained when the light reflected from the etalon is not allowed for,* and k is the coefficient which signifies the intensity increase due to this light.

*The intensity of the interference pattern at the point corresponding to A will be equal to B_0 if the point A_1 lies beyond the extent of the light source.

If we assume that all the points A_1 do not lie too close to the points in the focal plane F corresponding to maximum transmission of the etalon for monochromatic light, the coefficients τ_1 are approximately equal, that is, $\tau_1 = \tau$ and $k = 1/(1 - \tau)$. We shall make an estimate of the value of τ. Consider the case when the light source is an atomic beam. Let us assume that lens 2 (see diagram) serves simultaneously as the window of the vacuum chamber and that the spherical mirror 4 is inside the apparatus. For this case

$$\tau = (1 - r)^6 (1 - q)(1 - \chi) RR_{et.},$$

where r is the reflection coefficient of the surfaces of the condensing lens and the first surface of the first etalon plate (altogether there are three surfaces through each of which the light passes two times), the coefficient q allows for absorption of light in the condensing lens and in the first etalon plate, the coefficient χ indicates the loss of light resulting from self-absorption in the light source, R is the reflection coefficient of the spherical mirror, and $R_{et.}$ is the reflection coefficient for monochromatic light of the air-spaced Fabry-Perot etalon.



Let us suppose that r = 0.01 (it is assumed that two-layer antireflection coatings are used on the optical surfaces), q = 0.04 (assuming 1% absorption per cm of light path in glass and a total light path in both directions of 4 cm), R = 0.95, and χ = 0 (we assume that the self-sorption is small). One can assume $R_{et.}$ = 0.98 for etalon with dielectric mirrors at points away from t mission maxima. Then τ = 0.84 and $k = 1/(1 - \tau)$ =

When using reflected light to increase the intens of interference rings it is important to locate the po C and O correctly with respect to one another. It is expedient to choose a separation between C and O small as possible (as small as the instrumental widt of the etalon will permit). Furthermore, if the inter ence pattern is to be photographed, these points shou be located in such a way that the straight line CO is parallel to the slit of the spectrograph. In those cas when a narrow slit and a photoelectric method of re cording of the central spot are used it is more conve to place the straight line CO perpendicular to the sp trograph slit. With photoelectric recording it is furt desirable to use a separation between the points C a O such that the points A_1 which form an "image" o entrance aperture of the photomultiplier do not coinc with at least the interference ring closest to the cen for the case when the center of the interference patt corresponds to maximum transmission.

It is possible that for particularly accurate mea ments it might be necessary to consider the possibil of a small deformation of the contours of the interfe ence rings resulting from the use of reflected light. These deformations cannot cause changes in the loca tions of maxima on a record if the interference patte is recorded photoelectrically.

In order to avoid the shearing of light beams fo cessive reflections from the etalon and the spherica ror it is necessary that the distance l between the c densing lens and the first etalon plate be equal to f[(f/r)] where f is the focal length of the condenser a is the radius of curvature of the spherical mirror.*

*If we use a system consisting of a lens and a plane ror in place of the spherical mirror the condition be comes l = f.

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TABLES OF FRESNEL'S COEFFICIENTS FOR ABSORBING MEDIA

A. P. Prishivalko, G. M. Busak, and I. L. Onichek (pp. 555-556)

Received 4 May 1961

The study of reflecting power provides important in-
ation in regard to the optical properties of a sub-
e. In order to obtain a complete interpretation of
pectrum of reflection of an absorbing medium it is
ntial to know the dependence of the reflection factor
e relative index of refraction n, the absorption in-
, the angle of incidence, and the polarization of the
ent wave. This dependence yields the well-known
nel equations. However, the complex nature of the
of refraction ($m = n - i\kappa$) makes this dependence
complicated in the case of absorbing media.
The Fresnel equations were reduced by König[1] to the
wing form for absorbing media:

$$R_s = \frac{a^2 + b^2 - 2a\cos\varphi + \cos^2\varphi}{a^2 + b^2 + 2a\cos\varphi + \cos^2\varphi}, \quad (1)$$

$$R_p = R_s \frac{a^2 + b^2 - 2a\sin\varphi\tan\varphi + \sin^2\varphi\tan^2\varphi}{a^2 + b^2 + 2a\sin\varphi\tan\varphi + \sin^2\varphi\tan^2\varphi}, \quad (2)$$

$$a^2 + b^2 = \sqrt{(n^2 - \varkappa^2 - \sin^2\varphi)^2 + 4n^2\varkappa^2}, \quad (3)$$

$$= \sqrt{\frac{1}{2}\left[n^2 - \varkappa^2 - \sin^2\varphi + \sqrt{n^2 - \varkappa^2 - \sin^2\varphi)^2 + 4n^2\varkappa^2}\right]}. \quad (4)$$

ere R_s and R_p are the reflection factors for two
lly perpendicular directions of polarization of the
ent light, φ is the angle of incidence, n is the
ve index of refraction, and κ is the ratio of the
ption index of the second medium to the index of
ction of the first on condition that the first medium
nsparent.
Formulas (1)-(4) are complicated enough to make
utations with them very laborious. However, the
ction between the spectrum of reflection of a sub-
e and its optical properties can be established only
e basis of analysis of the relations (1)-(4).
n practice it is important to be able to determine
otical constants n and κ from measurements of
ent characteristics of reflection. Values of the re-
on factors at two different angles of incidence, the
meters of elliptic polarization of reflected light, the
s parameters, etc., can be selected as measured
ities. The relationships of these quantities acquire
re or less simple form only in certain special cases.
majority of cases it will be necessary to resort to
abulation of formulas (1)-(4) and the application of
ous graphical methods. In this instance it will always
ecessary to carry out cumbersome computations,
the results of which usually remain the property of a few persons. As yet we know only the work of Gol'man and Stepanov[2] which contains tables of the reflection factors of absorbing media. However, these tables are not sufficiently complete, since they have been compiled for only nine angles of incidence and contain only energy coefficients of reflection. They were publishes in an edition which came out in very few copies and are difficult to obtain.

For this reason we have undertaken new computations of reflection factors which were carried out on the "Ural" electronic computer in the Institute of Mathematics and Computational Techniques. The computations were carried out twice with two programs. One of these was written in fixed point, the other in floating point arithmetic. When the results of these two computations were compared, their coincidence was established with an accuracy to at least four decimal places. Tables of the amplitude and energy reflection factors were compiled on the basis of the data obtained: $r_s = A_s + iB_s$; $r_p = A_p + iB_p$; $R_s = r_s r_s^*$; $R = r_p r_p^*$. The tables include 26 values of the index of refraction n equal to 0.1 (0.1) 1.0 (0.2) 3 (0.5) 4 (1) 6 (2) 10, and 28 values of the absorption index κ equal to 0 (0.02) 0.1 (0.1) 1 (0.2) 2 (0.5) 4 (1) 6 (2) 10, for 17 angles of incidence φ equal to 0° (10°) 30° (5°) 80° (2.5°) 87.5°. The tables were compiled with an accuracy to 0.0001 and comprise on the order of 15-18 printed sheets.

The fact that the tables contain values of both the energy and amplitude reflection factors makes it possible to compute different characteristics of elliptic polarization of reflected light, the phases of reflected components, the azimuth of restored polarization, the values of the four Stokes parameters, the degree of polarization, etc. The tabulated data for $n < 1$ and $\kappa = 0$ permit one to draw certain conclusions as to the nature of total internal reflection.

These tables are in the possession of the Institute of Physics, Academy of Sciences, Belorussian SSR.

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USE OF A FABRY-PEROT ETALON FOR STUDYING SPECTRAL LINE WIDTHS IN PULSED DISCHARGES

V. G. Koloshnikov, M. A. Mazing, S. L. Mandel'shtam, and Yu. P. Marasanov (pp. 556-558)

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In the study of pulsed discharges the investigation of spectral line widths during the period of the discharge is of great interest, since in this way the kinetics of the temperature rise of the ions of the plasma can be delineated. The problem can be solved by using a photographic method in conjuncation with various systems of time scanning. For a number of problems a mirror scan or Kerr shutter is quite satisfactory and allows one to obtain essential data. However these methods, each of which has its own advantages, have a common intrinsic disadvantage, namely, their low light sensitivity. This disadvantage is the deciding factor in studying pulsed discharges in chambers with small amounts of contaminants (as, for example, the Tokomak-2 chamber). In order to obtain with such a chamber a spectrogram with a time scan and normal photographic blackening on an instrument possessing sufficient dispersion for line width measurements, several hundred discharges would undoubtedly be required; this would be very difficult in practice.

We have solved the problem using a photoelectric arrangement with a Fabry-Perot etalon as the spectral dispersing element. As is well-known[1] the light power for a given resolution with a Fabry-Perot etalon is much greater than for a monochromator, the gain amounting to two orders of magnitude. The light intensities were measured with a photomultiplier and the spectral line was scanned by altering the spacing of the etalon. In our arrangement the piezoelectric properties of barium titanate were used for moving one of the etalon plates.* The

*As we were informed by A. A. Varchenko after our lecture at the Twelfth All-Union Conference on Spectroscopy, a similar method was used by V. V. Kandiba and his coworkers.

etalon plate was attached to the end of a ceramic tube made of barium titanate. A voltage of 5 kv on the ceramic displaced the etalon plate by 3-4 μ from its position with no potential difference on the ceramic. The profile of the line was recorded by rapidly removing the voltage from the ceramic. The speed of removal of the voltage was fixed by the time constant of the discharge of a condenser connected in parallel with the coated surfaces of the ceramic. The discharge of the condenser was initially synchronized with the discharge in the chamber under study by means of a special multichannel circuit which gave, on the output side of the various channels, pulses displaced from one another in time. This displacement could be smoothly varied from zero to 50 msec. During a single discharge from 3 to 8 consecutive profiles of the line were recorded. The minimum time interval required for recording a single profile was about 50 μsec. It would undoubtedly be difficult to decrease this time interval.

The method described was given a preliminary trial by recording the 5461 A line of mercury (Fig. 1). The half-width of the line obtained agreed to within 10% with

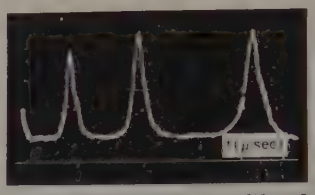

Fig. 1. Oscillogram of the profile of the 5461 A line of mercury. The light source was a PRK-4 mercury lamp.

the value obtained by the usual photographic method. method was then used to record the profiles of the H_β and CIII lines in spectra of the discharge in the toroi chamber "Tokomak-2." Figure 2 shows an oscillogr of the profile of the H_β line. The width of the apparat function of the etalon in this case was determined by cording the profile of the 5461 A line of mercury in t spectrum of a DRS-20 lamp; its value was 0.8 A. The width of the observed profile, averaged from 10 oscil grams and over the period of the discharge, was 2 A. it is assumed that the true profile of the spectral line has a Doppler shape, the apparatus function of the eta can be eliminated by using the calculations given in r 2. One then obtains 1.7 A for the half-width of the lin

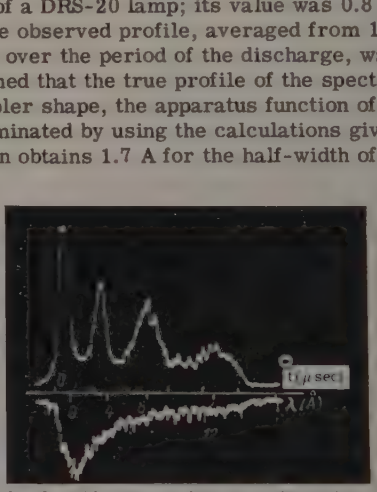

Fig. 2. Oscillogram of the profile of the H_β line (upper curve). The lower curve shows the intensity variation of the line during the period of the discharge.

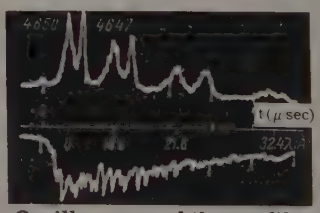

Fig. 3. Oscillograms of the profiles of the CIII 4647.40 and 4650.16 A lines (upper curve). The lower curve shows the intensity variation of the line during the period of the discharge.

e 3 shows oscillograms of the CIII 4647.40 and
16 A lines. For this recording the apparatus func-
f the etalon was 1.4 A. The observed width, aver-
rom 10 oscillograms for the 4650.14 and 4647.40 A
was 1.8 A. After eliminating the apparatus func-
ne value obtained for the half-widths of the lines
.7 A.

he authors express their gratitude to N. A. Yavlinskii and G. G. Dolgov-Savel'ev for their interest in the work and their valuable advice.

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ETERMINATION OF DEUTERIUM IN WATER AT CONCENTRATIONS CLOSE TO THE NATURAL ABUNDANCE ON THE BASIS OF INFRARED ABSORPTION SPECTRA

V. A. Borgest (pp. 558-559)

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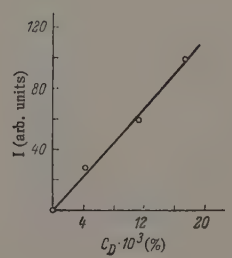
he spectroscopic methods known at the present for the determination of small quantities of deu- in water do not provide the necessary accuracy natural deuterium content (0.015%) and have not sed for the analysis of still lower concentrations. roposed method allows one to use a linear calibra- urve in the interval from 0.003 to 0.020% deuterium, n also be applied to the analysis of higher concen- ns.

he analysis is carried out by means of an IKS-6 ophotometer with NaCl prisms, provided with an optico-acoustical radiation detector. The signal, ated at a frequency of 9 cycles, is amplified, is ed by a synchronous detector, and passes into an 09 recording potentiometer with a 10-mv scale. sorption band of the OD stretching vibration of O molecule, located at about 2500 cm^{-1}, is chosen analytical band. The wavelength drum is fixed in sition corresponding to maximum absorption in the region, and the spectrum is not scanned. The cell, kness 460 μ with a quartz ring and fluorite win- is filled with the water samples to be analyzed h openings drilled in one of the windows.

y the use of an amplification factor which is high parison with the usual working conditions, and by g the spectrophotometer slits, the signal entering corder is brought to a value amounting to approxi- 150 mv. The difference between the apparatus gs corresponding to two different deuterium con- tions close to the natural value then proves to be ient for measurement with an accuracy determined stability of the detecting-recording part of the ap- s. To avoid overloading the latter stages of the am- , and also to retain the EPP-09 as the recording , a compensating alternating voltage of the same ency but opposite phase is fed to the control grid of cond stage of the amplifier together with the work- gnal. The magnitude of this voltage is held constant he necessary stability, is exactly known each time, chosen in such a way that the excursions of the re- r pen remain within the limits of its scale.

sing the Beer-Lambert law for the intensities I_1 of the light which passes through water samples



with deuterium concentrations C_1^D and C_2^D, one can obtain

$$I_1 - I_2 = I_2(k^H - k^D)\, d\,(C_1^D - C_2^D).$$

Here d is the cell thickness, and k^H and k^D are the absorption coefficients of H_2O and HDO in the selected spectral region. This formula is valid under the condition that $I_1 - I_2 \ll I_2$. In our case this is justified, since $I \approx 100\,\Delta I$. Allowance for scattered light leads to the formula's taking the following form:

$$I_1^{obs.} - I_2^{obs.} = I_1 - I_2 = (I_2^{obs.} - I^{scat.})\, d\,(k^H - k^D)(C_1^D - C_2^D).$$

Here I_1 and I_2 have their previous meanings, $I^{scat.}$ is the intensity of the scattered light, and $I_1^{obs.}$ and $I_2^{obs.}$ are the observed intensity values. Thus the curve of the function $I = I(\Delta C^D)$ is linear and passes through the origin. Standard samples are made up by weighing from water containing not more than 1×10^{-5}% deuterium and from 1% deuterium oxide. The calibration curve constructed for the interval 0-0.18% deuterium is represented in the Figure. For $C^D = 0.015$%, the relative mean square error of a single measurement, which is composed of the error in determining the slope of the curve, as calculated according to the method of least squares, and of the error in determining the intensity as obtained by averaging the deviations of the experimental data from those computed according to the curve, amounts to 7%, which exceeds the precision of mass-spectrometric water analysis.[3] In the work cited above,[1] the relative error in the determination of deuterium in natural water amounts, according to the author's esti-

mate, to 2%. However, analysis of the tables presented in the article permits one to conclude that this precision is greatly overstated. Actually, even if we admit that the parameters of the calibration curve are determined with complete reliability, still, on account of its small slope (90 mv/1% D_2O), the error in the intensity determination (0.25 mv) as presented in the article corresponds to an error of 0.0028% in the determination of C^D, which amounts to 15% on a relative basis for the natural concentration. The precision indicated in ref. 1 characterizes not the error in determining the concentration, the reproducibility of the intensity measurement.

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EVENTS

THE SECOND CONFERENCE ON THE PHYSICS OF ALKALI HALIDE CRYSTALS

Reported by Ch. B. Lushchik and K. K. Shvarts (pp. 560-562)

The Second Conference on the Physics of Alkali Halide Crystals took place in Riga from the 19th to the 24th of June, under the auspices of the Scientific Committee on Luminescence of the Academy of Sciences of the USSR, the Latvian State University, and the Institute of Physics of the Academy of Sciences of the Latvian SSR. More than 200 people from 19 cities in the Soviet Union took part in the conference. Ninety reports devoted to the optical, electrical, magnetic, dielectric, mechanical, and physico-chemical properties of alkali halide crystals, as well as theory of ionic crystals, were heard at the joint and sectional meetings of the conference.

The central theme of the conference was the many-sided investigation of the microstructure of alkali halide crystals and the micromechanisms involved in their physical processes. The results of studies which are most essential for establishing relationships between the point, line, and surface defects of the crystals on the one hand and the optical, electrical, mechanical, etc., properties of the crystals on the other were presented at the conference. Particular attention was directed to the effects of various kinds of radiation and particles on the characteristics of alkali halide crystals.

Since it is not possible to examine all the papers presented at the conference, we will limit ourselves to a brief summary of the fundamental studies devoted to the optical properties of alkali halide crystals.

A report by A. I. Stekhanov entitled "Raman Scattering of Light in Alkali Halide Crystals" was received with interest. This paper contained a very find experimental demonstration of the existence of local oscillations in alkali halide crystals near defects in the crystal lattice.

A broad survey by P. P. Feofilov and A. A. Kaplyanskii was devoted to hidden optical anisotropy of cubic crystals containing local centers, and the methods used to study it. The speakers successively examined models of local anisotropic centers in cubic crystals, anisotropy of absorption and emission of light, multipolarity of elementary radiators, etc. Considerable attention was paid to the detection of the concealed anisotropy of centers by means of oriented elastic deformation of the crystals and the use of external magnetic and electric fields. Particular interest was stimulated by the presentation of the characteristics of impurity centers having line spectra in several ionic crystals, which are known to have very important applications as quantum generators in the optical band of the spectrum. The piezospectroscopic fect of uranium ions in alkali fluoride crystals was cussed in detail in an accompanying report by A. A. Kaplyanskii and N. A. Moskvin.

A large number of reports were devoted to the troscopic and physico-chemical study of luminescer centers in ionic crystals activated by different impu ions.

New results regarding the spectral characteris of "mercurylike centers" in alkali halide, oxide, ar phosphate luminors which are activated with Ga^+, G In^+, Sn^{2+}, Sb^{3+}, Tl^+, Pb^{2+}, and Bi^{3+} ions were presente a report by Ch. B. Lushchik, N. E. Lushchik, S. G. Zazubovich, and I. A. Muug. The main emphasis wa placed on the polarization characteristics of the cer which indicated that the oscillators involved in the r ation are electric linear dipoles oriented along the axis.

I. K. Plyavin, M. F. Trinkler, A. K. Evert, and Ya. Zund examined the kinetics of intracenter proce in crystal phosphors activated with mercurylike ion and showed in particular that, for indium and galliu phosphors, the duration of the photoscintillations ch by the same law as the quantum yield in the region thermal quenching.

R. I. Gindina discussed the microstructure and nescence centers of several alkali halide crystal ph phors. Spectroscopic and microscopic studies led h the conclusion that the primary luminescence is not calized at the grain boundaries. It was shown that p microdefects produced by x-rays and ultraviolet ra tion increased the number of complex luminescence ters.

The relationship of concentration and thermal quenching in alkali halide crystals was discussed in report by L. A. Rebane.

F. D. Klement and L. A. Teiss reported on the tral characteristics of impurity centers in composi alkali halide crystals of CsCl·CsBr-Pb. The resul tained confirm the ideas developed by the speakers cerning the presence of different isostructures of i purity centers in composite crystals.

A lively discussion was stimulated by the inter report of N. I. Ivanova, L. I. Tarasova, and A. P. Z skii in which the possibility of the existence of lum cence centers in the form of complexes in alkali ha crystals was considered.

In a report by M. U. Belyi and his co-workers, the tral characteristics of several alkali halide crystal phors and frozen liquid solutions of different ions compared. O. A. Shmit et al. discussed "anion im- y centers" in crystals containing S^{2-}, Se^{2-}, etc. The spectral characteristics and possible micro- ture of complex luminescence centers in alkali e crystals which form when there is a high concen- on of activators and other microdefects were con- ed in reports by T. A. Abdusadykov, A. N. Panova ., A. Kh. Khalilov and co-workers, and E. I. Shura- The results presented in these papers and also in eport by V. I. Vishnevskii, A. B. Lyskovich, M. L. yrailo, and Z. L. Chorniya are of value in the de- oment of scintillation counters for nuclear radiation. The gamma-, x-ray-, photo-, and thermolumines- e spectra of "pure" alkali halide crystals were dis- ed by N. N. Vasil'eva and Ya. A. Valbis. The spectral characteristics of alkali halide crys- activated with nickel were examined in detail in re- s by I. A. Parfianovich, M. L. Kats and B. Z. Seme- L. M. Shamovskii and N. D. Maksimova. The spec- nd microstructure of atomic activator color centers rayed and additively colored crystals containing sil- nd copper were discussed in reports presented by aratov group of M. L. Kats and also by L. M. Sham- i and A. S. Shibanov.

A. A. Shatalov and his co-workers reported having ed the microstructure and the aggregation mecha- of F-centers in additively colored crystals by po- ation, electron microscopic, and paramagnetic ods.

A. A. Shatalov, M. A. Ruban, and A. A. Bugai de- d the fine structure of the electron paramagnetic nance spectrum in KCl crystals at 20°K. Micro- rtions of the crystal lattice of ionic crystals near ign" ions (Ag^+ for example) which were detected the aid of nuclear paramagnetic resonance were ssed in a report by M. I. Kornfel'd and V. V. Le- v. This paper stimulated a great deal of interest. A group of reports was devoted to the optical in- gation of the electronic, hole, sensitization, ionic, cation, and other physical processes in alkali halide als.

Ch. B. Lushchik gave a survey of the investigations e migration of energy in alkali halide crystal phos- s which have been carried out at Tartu. Study of the us spectra and of the action of ultraviolet radiation e absorption, luminescence, and electrical charac- tics of the crystals has made it possible to obtain mation on the micromechanism of the migration of gy between impurity centers, from impurity cen- to the host material, and from the host material to mpurity centers.

The nature of the luminescence of alkali halide crystal phosphors under excitation by x-rays and gamma rays was discussed in reports by L. M. Shamovskii and T. A. Soovik. The report "Colorability and Luminescence of NaCl and KCl Phosphors" by I. A. Parfianovich considered the effect of dislocations on several physical processes in ionic crystals, and also discussed the mechanism of recombination luminescence in ionic crystals.

Absorption methods were brought in for a study of the photothermal ionization of F-centers (F. N. Zaitov, Yu. L. Lukantsever) and the processes of dissociation of solid solutions (E. K. Zavadovskii, I. Ya. Melik-Gaikazyan, L. V. Grigoruk).

A thorough investigation of the luminescence which arises when ionic crystals are shattered was carried out by L. M. Belyaev and his co-workers.

An interesting group of reports was devoted to the theory of ionic crystals.

K. B. Tolpygo gave a detailed review of the studies on the zone structure of alkali halide crystals and its connection with the properties of impurity centers, excitons, and polarons. The primary interest was aroused by the author's original results on the structure of the hole zone and the theoretical interpretation of the effect of autolocalization of holes in ionic crystals.

In a survey, M. I. Petrashen' discussed the results of investigations carried out over several years by himself and his co-workers on quantum mechanical computations of electron centers with small radii in ionic crystals. Methods of determining the wave function of the electron motion, methods of microcalculation of the adiabatic potentials of the center, and finally the results obtained when computing specific models of impurity centers were examined in detail.

The report of N. N. Kristofel' and K. K. Rebané was devoted to the interaction of electrons of the impurity center with lattice vibrations. The main emphasis was placed on a theoretical examination of the question of the existence of local oscillations in crystals with impurity centers and their interaction with the crystal vibrations.

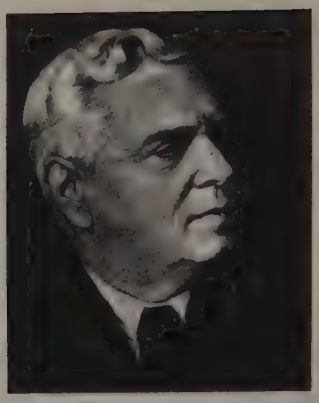
Z. A. Demidenko and K. B. Tolpygo presented a paper on the dispersion of natural frequencies in the theory of alkali halide crystals with deformed ions.

The Riga conference demonstrated that spectroscopic and especially luminescence methods are very effectively employed for clarification of the microstructure of ionic crystals and the investigation of the most diverse occurrences in their physical processes. The rapid development of the spectroscopy of alkali halide crystals is connected first of all with the fact that ionic single crystals have taken on exceptionally important application during the last decade (scintillators, quantum generators, etc.) and, like semiconductors, have now passed into the domain of industrial exploitation.

OBITUARY

N. N. KACHALOV

(pp. 563-564)



The prominent Soviet scientist, Professor Nikolai Nikolaevich Kachalov, recipient of the Stalin Prize, esteemed worker in science and engineering in the RSFSR, and corresponding member of the Academy of Sciences of the USSR, died on June 19, 1961.

The fundamental stages in the development of the science of glass in our country and the large-scale successes in the domestic production of optical glass are closely associated with the name of N. N. Kachalov.

After completing his studies at the St. Petersburg Mining Institute in 1911, N. N. Kachalov worked at the China Factory (now the Lomonosov Works), where he carried out his first experimental investigations, developing the technology of the manufacture of soft porcelain and also organizing the production of technical porcelain, which was not then being made in Russia. The First World War which began in 1914 confronted the factory with the task of setting up the production of domestic optical glass, which had previously been imported from abroad. By the exertions of N. N. Kachalov, who by that time had become technical director of the China Factory, an optical shop was founded and the first successes in the manufacture of optical glass were achieved. He resumed this work, interrupted by civil war, in 1923, when the optical shop of the China Factory was reorganized as the Lenzos factory.

On his initiative, experimental work leading to the elaboration of a new progressive method of melting optical glass was broadly developed at Lenzos both by himself and by a large group of scientists—D. S. Rozhdestvenskii, I. V. Grebenshchikov, and others. Thus the problem of the production of high-quality optical glass in the SSSR was finally solved, and after 1927 was no longer imported.

N. N. Kachalov took an active part in the organization of the State Ceramic Institute, in which, on his introduction, the study of domestic silicate raw materials was carried out over a number of years.

For many years he was associated with the State Optical Institute in which he worked at first as deputy director, then as chief of the laboratory and as consultant. Here he planned and constructed a special experimental glass works where he carried out investigations on the improvement of the technology of optical glass production.

The professorial activity of N. N. Kachalov in the Leningrad Technological Institute, where he headed the section of glass technology which was organized by him, began in 1930. N. N. Kachalov united his pedagogic work with extensive scientific investigations of the most urgent questions of glass technology. A profound study of the processes of glass grinding and polishing was carried out under his direction. During his time in the glass section, the synthesis of new technical glass was accomplished; the methods of working their surfaces were studied and new fields for the application of glass were found (decorative glass and glass sculpture).

In 1948, N. N. Kachalov took an active part in the organization of the Institute of Silicate Chemistry of the Academy of Sciences of the USSR, where he worked for several years as deputy director, heading the laborat of the cold working of silicate materials. In this last period of his life, he directed studies on the physical physicochemical nature of the processes of the grindi and polishing of glass and other brittle materials, and carried out a broad plan to introduce the results of hi many years' work into factories making polished plat glass. On his initiative, coordinating conferences of s cialists, research associates, and engineers working the field of glass grinding and polishing were systema cally called in to the Institute of Silicate Chemistry of Academy of Sciences of the USSR over a number of ye

N. N. Kachalov was the author of a number of mo graphs, manuals, and books. His monograph "Funda- mentals of the Processes of Glass Grinding and Polis ing" (1946) was honored with the Stalin Prize. The m ual "Technology of Glass Grinding and Polishing" (19 and his crowning work "Glass," which appeared in 19 and represented its author's half-century of activity i the theory and practice of glassworking, are widely known among specialists in the USSR and beyond our borders. The latter book is a model of popular scient literature. In it, against a background of the developm of human society over many centuries, N. N. Kachalo sets forth the history of the origin and progress of de velopment of glass, and presents in a clear and signif cant form the basic concepts concerning the nature of glass, its properties, and the diverse technology of it manufacture.

For a number of years, N. N. Kachalov was elect as a representative of the Frunze region, and later of Leningrad City and District Councils of Worker's Rep sentatives. The brilliant publicizing activity of this s entist is well known; he remembered well the most in portant events of our time, and he devoted great effor to the education of Soviet youth, showing it by the exa ple of the bright pages of his own life, the fascination creative work for the good of the Soviet Motherland.

For his outstanding merits in the development of Russian science and engineering, N. N. Kachalov was rewarded with the Order of Lenin, with two Orders of the Red Banner of Labor, with the Order of the Red S and with many medals.

APPLIED OPTICS

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ABBREVIATIONS FOR JOURNALS, PLACES, ETC. OFTEN REFERRED TO IN "OPTICS AND SPECTROSCOPY"**

Doklady Akad. Nauk SSSR - Proceedings of the Academy of Sciences of the USSR

Izvest. Akad. Nauk SSSR - Bulletin of the Academy of Sciences of the USSR
Ser. Fiz. - Physical Series
Ser. Mat. - Mathematical Series
Otdel Khim. Nauk - Chemical Sciences Section

Uspekhi Fiz. Nauk - Advances in Physical Sciences

Uspekhi Khim. - Advances in Chemistry

Zhur. Eksptl. i Teoret. Fiz. - Journal of Experimental and Theoretical Physics

Zhur. Tekh. Fiz. - Journal of Technical Physics

Zhur. Obshchei Khim. - Journal of General Chemistry

Zhur. Priklad. Khim. - Journal of Applied Chemistry

Zhur. Russ. Fiz.-Khim. Obshchestva - Journal of the Russian Physical-Chemical Society

Zhur. Fiz. Khim. - Journal of Physical Society

Trudy Fiz. Inst., Akad. Nauk SSSR, Fiz. Inst. im. P.N. Lebedev - Transactions of the Institute of Physics, Academy of Sciences of the USSR, named for P.N. Lebedev

Trudy Fiz.-Tekh. Inst., Akad. Nauk Uzbek. SSR - Transactions of the Physico-Technical Institute, Academy of Sciences of the Uzbek SSR

Trudy Inst. Krist., Akad. Nauk SSSR - Transactions of the Institute of Crystallography, Academy of Sciences of the USSR

Trudy Inst. Nefti, Akad. Nauk SSSR - Transactions of the Petroleum Institute, Academy of Sciences of the USSR

Trudy Gosudarst. Opt. Inst., Leningrad - Transactions of the Optical Institute in Leningrad

Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. SSR - Transactions of the Institute of Physics and Astronomy, Academy of Sciences of the Estonian SSR

Trudy Inst. Fiz., Akad. Nauk Ukr. SSR - Transactions of the Institute of Physics, Academy of Sciences of the Ukrainian SSR

Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol. - Transactions of the All-Union Scientific Research Institute of Meteorology

Vestnik Leningrad. Univ. - Bulletin of the Leningrad University
Ser. Fiz. i Khim. - Series on Physics and Chemistry

Gosudarst. Opt. Inst. - State Optical Institute

Moskov. Fiz.-Tekh. Inst. - Moscow Physico-Technical Institute

Izd. Inostrannoi Lit. - Publishers of Foreign Literature

Izd. Akad. Nauk SSSR - Academy of Sciences Press

Vestnik Moskov. Univ. - Bulletin of Moscow University
Ser. Fiz.-Mat. i Estestven. Nauk - Series of Physical-Mathematical and Natural Sciences

Uchenye Zapiski Leningrad. Gosudarst. Univ. im. A. A. Zhdanov - Scientific Reports of the Leningrad State University named for A. A. Zhdanov
Ser. Fiz. Nauk - Series on the Physical Sciences
Ser. Khim. Nauk - Series on the Chemical Sciences

Uchenye Zapiski, Moskov. Gosudarst. Univ. im. M. V. Lomonosova - Scientific Reports, M.V. Lomonosov Moscow State University

Uchenye Zapiski Tomsk. Gosudarst. Univ. in. V. V. Kuibysheva - Scientific Reports of the Tomsk State University named for V. V. Kuibyshev

Opt. i Spektr. - Optics and Spectroscopy

Pribory i Tekh. Ekspt. - Instruments and Technique of Experiment

Astron. Zhur. - Astronomical Journal

Fiz. Metal. i Metalloved., Akad. Nauk SSSR, Ural. Filial Physics of Metal and Metallography, Academy of Sciences of the USSR, Ural Branch

Priborostroenie - Instrument Manufacturing

Zavodskaya Lab. - Factory Laboratory

Radiotekhnika - Radio Engineering

Radiotekh. i Elektron. - Radio Engineering and Electroni

Inzhener.-Fiz. Zhur., Akad. Nauk Belorus. SSR - Engineering-Physics Journal, Academy of Sciences of White Russian SSR

Ukrain. Fiz. Zhur. - Ukrainian Physics Journal

Automat. i Telemekh. - Automatics and Telemechanics

Nauch.-Issledovatel. Fiz.-Tekh. Inst., Leningrad. Univ. - Scientific Research Institute of Physics and Technology, Leningrad University

Nauch.-Issledovatel. Radio-fiz. Inst., Gor'kii Univ. - Scientific Research Institute of Radiophysics, Gorki University

Gorkov. Issledovatel. Fiz. Tekh. Inst. - Gorki Research Institute of Physics and Technology

Gosudarst. Izd. Tekh.-Teoret. Lit. - State Publishers of Technical-Theoretical Literature

Gosudarst. Izd. Fiz.-Mat. Lit.- State Publishers of Physical-Mathematical Literature

Inst. Fiz., Akad. Nauk Ukr. SSR, Kiev - Institute of Physic Academy of Sciences of the Ukrainian SSR, Kiev

Inst. Fiz. i Astron., Akad. Nauk Eston. SSR, Tartu - Inst tute of Physics and Astronomy, Academy of Science of the Estonian SSR, Tartu

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